378.744
BO
AM 1933
S

Boston University
College of Liberal Arts
Library

THE GIFT OF The Author

378.744
BO
A.M. 1933
S

p7573

BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

PREPARATION OF META TOLUENE SULFONIC ACID FROM META TOLUIDINE

by

Samuel David Schwartz

(B.CH.E., Northeastern University, 1932)

submitted in partial fulfilment of the

requirements for the degree of

Master of Arts

1933

BOSTON UNIVERSITY
COLLEGE OF LIBERAL ARTS
LIBRARY

P4543

378.744
BO
AM 1933
S

PREFACE

The specific purpose of this research is to prepare meta-toluene sulfonic acid from meta-toluidine. It was proposed that aromatic sulfonic acids could be prepared from the toluidines by first preparing the sulfinic acids and then oxidising them to the sulfonic acids. Although it has been stated in the literature that this has been prepared, the method has not been published as far as the author knows, and as a result this research may be of value for establishing a method for the isolation of this organic acid in a pure state which might be utilized as such for other organic preparations. The available knowledge on the oxidation of sulfinic acids is also very minute and it is hoped that this thesis will add to this knowledge.

The author wishes to acknowledge his indebtedness to Dr. J. P. Mason of Boston University for the encouragement, constructive criticism, and helpful guidance which he so eagerly and earnestly offered throughout this entire investigation. The author also wishes to thank Mr. I. Schwartz for his aid in the translating and abstracting of the many German articles used as references for this thesis.

TABLE OF CONTENTS

PAGE

Preface

Table of Contents.....1

Introduction.....3

Resume of the Literature.....9

Constitution of Sulfinic Acids.....12

Methods of Preparing M-Toluene Sulfonic Acids.....15

Preparation of Sulfinic Acids from Toluidine, According to Gatterman's Method.....17

Improved Methods of Preparing the Sulfinic Acids.....21

Experimental.....24

Apparatus.....24

Diagram of Apparatus (Fig. 1).....25

Procedure.....26

Addition of Sulfur Dioxide.....28

Isolation of P-Toluene Sulfinic Acid as the Iron Salt.....29

Diagram of Cooling Apparatus (Fig. 2).....30

Observations.....33

Preparation of M-Toluene Sulfinic Acid.....36

Procedure.....37

Observations.....40

Derivative of M-Toluene Sulfinic Acid.....44

Oxidation of Organic Compounds.....46

Oxidation of P-Toluene Sulfinic Acid to the Sulfonic Acid.....49

TABLE OF CONTENTS

PAGE

Preface

Table of Contents.....i

Introduction.....3

Review of the Literature.....9

Constitution of Sulfinic Acids.....12

Methods of Preparing P-Toluene Sulfonic Acids.....15

Preparation of Sulfinic Acids from Toluidine.

According to Gattermann's Method.....17

Improved Methods of Preparing the Sulfinic Acids.....21

Experimental.....24

Apparatus.....24

Diagram of Apparatus (Fig. 1).....25

Procedure.....26

Addition of Sulfur Dioxide.....28

Isolation of P-Toluene Sulfinic Acid as the Iron

Salt.....29

Diagram of Cooling Apparatus (Fig. 2).....30

Observations.....32

Preparation of P-Toluene Sulfinic Acid.....35

Procedure.....37

Observations.....40

Derivative of P-Toluene Sulfinic Acid.....44

Oxidation of Organic Compounds.....46

Oxidation of P-Toluene Sulfinic Acid to the

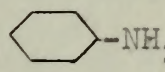
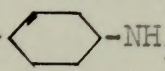
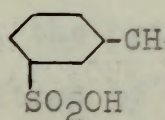
Sulfonic Acid.....49

Derivative of P-Toluene Sulfonic Acid.....56
Oxidation of M-Toluene Sulfinic Acid to the
Sulfonic Acid.....57
Derivative of M-Toluene Sulfonic Acid.....58
Solubility Table of P-Toluene Sulfonic Acid.....59
Possibilities for Future Research.....60
Summary and Conclusions.....62
Bibliography.....63

INTRODUCTION

The field of organic chemistry has grown extensively during the last twenty years and much work has been done to make this a very important branch of the science of chemistry. Together with the advanced knowledge concerning theoretical chemical principles and knowledge concerning the structure of the chemical atoms, organic chemistry has found many varied and wide applications in the industry as well as serving in the capacity of being a very interesting field for pure research.

As many organic chemists have pointed out, the dye industry is greatly indebted to the field of organic chemistry, and through the study of the constitution of natural coloring matter and attempts to synthesize products which have properties similar to the natural substances, much information and knowledge was gained concerning the chemical structure of many different compounds. The dyes prepared synthetically are used in the photochemical industry and in the field of food chemistry for the determination of pH values as well as for dyeing textiles.

Two basic substances play an important role for the manufacture of synthetic dyes. They are aniline () and its homologues; such as toluidines, () and the sulfonic acids such as benzene sulfonic acid and its homologues, like meta-toluene sulfonic acid (). The sulfonic acid group imparts a property to the dye which is invaluable to its use. Nicholson (1) discovered that certain dyes, insoluble

(1) Cohen, J.B., "Theoretical Organic CHemistry," p. 528, Macmillan and Co., (1928)

INTRODUCTION

The field of organic chemistry has grown extensively during the last twenty years and much work has been done to make this a very important branch of the science of chemistry. Together with the advanced knowledge concerning theoretical chemical principles and knowledge concerning the structure of the chemical atoms, organic chemistry has found many varied and wide applications in the industry as well as serving in the capacity of being a very interesting field for pure research.

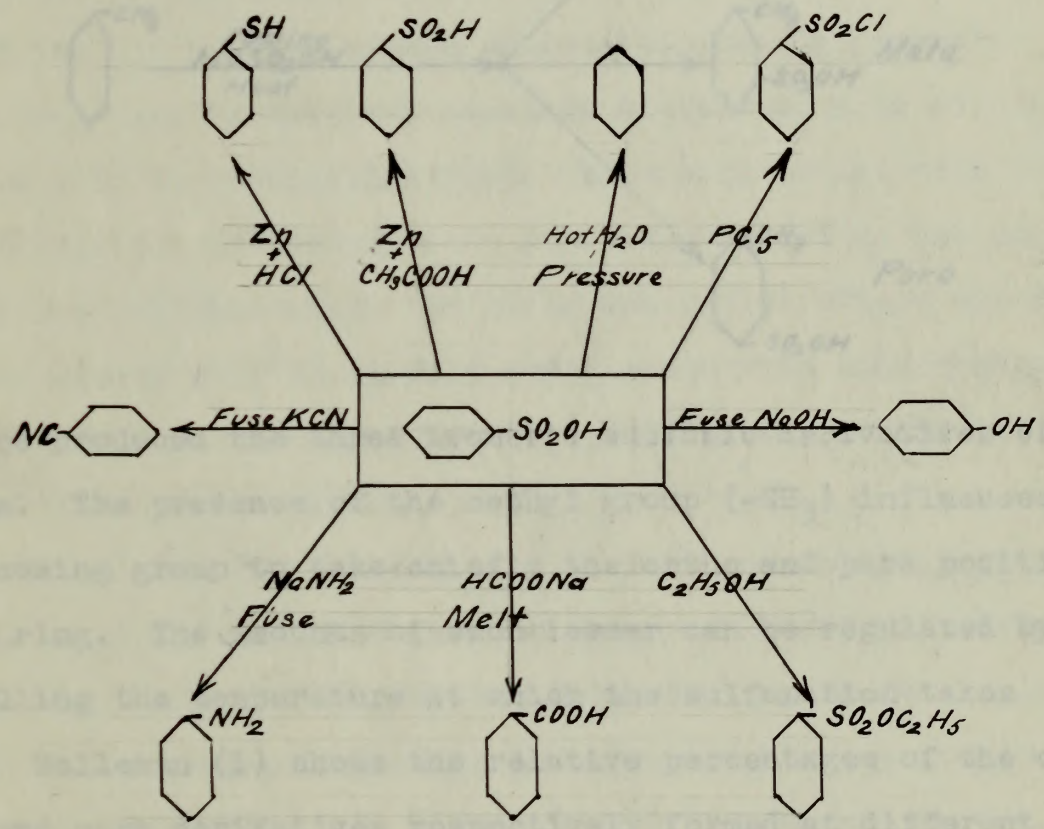
As many organic chemists have pointed out, the dye industry is greatly indebted to the field of organic chemistry, and through the study of the constitution of natural coloring matter and attempts to synthesize products which have properties similar to the natural substances, much information and knowledge was gained concerning the chemical structure of many different compounds. The dyes prepared synthetically are used in the photochemical industry and in the field of food chemistry for the determination of pH values as well as for dyeing textiles.

Two basic substances play an important role for the manufacture of synthetic dyes. They are aniline ($C_6H_5-NH_2$) and its homologues; such as toluidines, ($H_3C-C_6H_4-NH_2$) and the sulfonic acids such as benzene sulfonic acid and its homologues, like meta-toluene sulfonic acid ($C_6H_4(CH_3)(SO_3H)$). The sulfonic acid group imparts a property to the dye which is invaluable to its use. Nicholson (1) discovered that certain dyes, insoluble

(1) Cohen, J.B., "Theoretical Organic Chemistry," p. 528, Macmillan and Co., (1929)

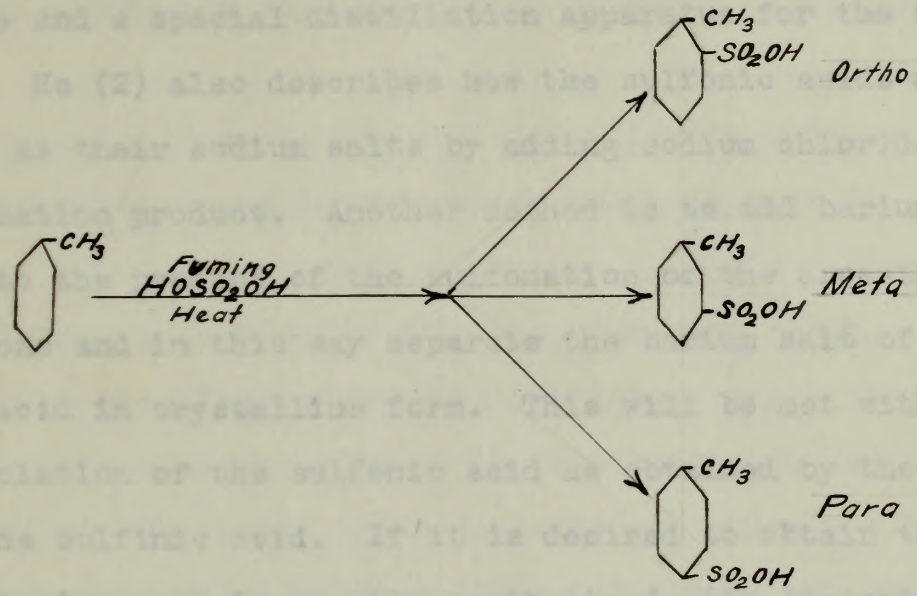
in water, on sulfonation, become soluble. The aromatic sulfonic acids may be used also for many other preparative purposes as indicated in Table I.

Table I.



The sulfonic acids can be prepared by direct sulfonation of the aromatic hydrocarbon, the hydrogen attached to the carbon of the ring being substitued by the sulfonic group ($-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$). Since this thesis is ultimately aiming at the preparation of the meta-toluene sulfonic acid, the direct sulfonation of

toluene ( ) will be taken as a typical reaction which is illustrated by the following reaction:



Thus are produced the three isomeric sulfonic derivatives of toluene. The presence of the methyl group ($-CH_3$) influences the incoming group to take chiefly the ortho and para positions in the ring. The amounts of each isomer can be regulated by controlling the temperature at which the sulfonation takes place. Holleman (1) shows the relative percentages of the ortho, meta, and para derivatives respectively formed at different temperatures on the sulfonation of toluene, shown by Table II.

Table II.

(a)	toluene	sulfonation 0° C	53 % p-toluene sulfonic acid 3.8 % m- " " " 42.7% o- " " "
(b)	toluene	sulfonation 100° C	72.5% p-toluene sulfonic acid 10.1% m- " " " 17.4% o- " " "

(1) Holleman, A.F., "A Text Book of Organic Chemistry," p. 467, John Wiley & Sons, Inc. (1930)

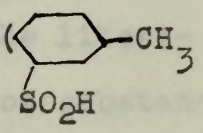
Gatterman (1) has described an ingenious apparatus for the isolation of the p-toluene sulfonic acid by the use of an excess of toluene and a special distillation apparatus for the removal or water. He (2) also describes how the sulfonic acids may be separated as their sodium salts by adding sodium chloride to the sulfonation product. Another method is to add barium chloride to the product of the sulfonation of the aromatic hydrocarbons and in this way separate the barium salt of the sulfonic acid in crystalline form. This will be met with later in the isolation of the sulfonic acid as obtained by the oxidation of the sulfinic acid. If it is desired to obtain the free acid the barium salt is exactly neutralized with concentrated sulfuric acid and the insoluble barium sulfate filtered off, and the filtrate evaporated.

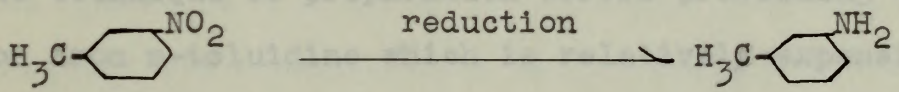
Still it can be seen that the relative amount of pure m-toluene sulfonic acid which can be prepared by direct sulfonation is small and the cost of obtaining it in pure form will be in most cases greater than will be warranted for its preparation on a commercial basis. As a result, any method devised by which each of the isomeric sulfonic acids could be obtained independently as pure isolated products would have scientific and possibly practical value.

The literature bearing directly on the preparation of m-toluene sulfonic acid is not very extensive and is noted in the respective places. This necessitates searching in a field parellel to the preparation of m-toluene sulfonic acid, namely

(1) Gatterman L. and Wieland., "Laboratory Methods of Organic Chemistry," p. 183-4. Macmillan Co., 1932.
(2) Gatterman L., Ber., 24, 2011-21 (1891)

the preparation of the ortho and para compounds from the starting point listed below. Thus a good deal of the resume of the literature deals with the preparation of these related compounds.

In order to prepare the m-toluene sulfonic acid, it was proposed to oxidize the corresponding sulfinic acid () to the sulfonic acid by some suitable oxidising agent, to be determined by experimental work in the laboratory. The starting point for the preparation of the sulfinic acid is to be the toluidine. The chief sources of the toluidine are from the chemical reduction of m-nitro-toluene (1) and by the electrochemical reduction of m-nitro toluene (2). The reduction for the formation of the toluidine is:



The general properties of the toluidine as reported in the Chemical Encyclopedia (3) are that the meta and ortho toluidines are liquids which boil at about 197.7 C and 203.3 C respectively. The p-toluidine is a white solid, lustrous substance, m.p. 45 C, from which many red, violet and blue dyes are made.

---

(1) Lowy, A. and Harrow, B., "An Introduction to Organic Chemistry," p. 239, John Wiley & Sons, Inc. (1932)
(2) Brockman, C.J., "Electro-Organic Chemistry," p. 234-5, John Wiley & Sons, Inc. (1926)
(3) Kingzett, C.T., "Chemical Encyclopedia," p. 924, P.Balliere, Tindall and Cox. (1932)

The specific method used in this research for the preparation of the sulfinic acid is that oultined by Gatterman (1) which consists in the diazotization of the corresponding toluidine at 0 C, saturating the solution with sulfur dioxide at 0 C and the addition of copper powder in the cold. Although this is the basic method, there are cited in the resume of the literature modifications of the procedure such as the use of substances other than copper powder to catalyze the reaction and various methods of isolating the free sulfinic acid.

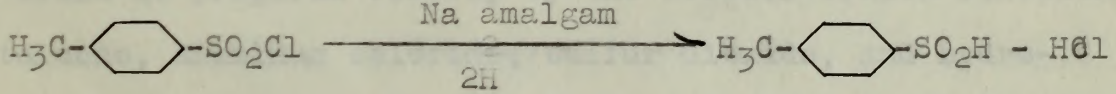
Oxidation methods for the transforming of the sulfinic acid to the sulfonic acid are purely experimental and the deductions therefrom are the individual observations of the investigator. The p-toluidine is used as the material from which the sulfinic and consequently the sulfonic acid are obtained in order to perfect the technique of preparation before proceeding with the preparation from m-toluidine which is relatively expensive.

(1) Gatterman, L., Ber., 32, 1136 (1899)

RESUME OF THE LITERATURE

The literature which pertains directly to the preparation of m-toluene sulfinic acid from which it is proposed to obtain the m-toluene sulfonic acid is very brief. Therefore this survey of the literature will deal with the sulfinic acids in a general way, and the different methods of preparing the sulfinic acids will be noted in addition to a detailed discussion of the principle method employed in this thesis in order to furnish as broad a view as necessary for a clear understanding of the field under observation.

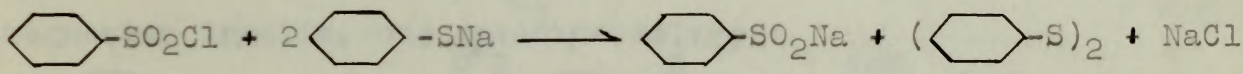
The sulfinic acids are organic acids which have the general formula R-S(=O)-H or R-S(=O)-OH depending on the view one takes concerning the structure of the acid. The nature of the constitution of the sulfinic acids will be discussed later. The sulfinic acids have been prepared by several general methods, which were discovered independently by different men. R. Otto (1) prepared p-toluene sulfinic acid by the reduction of p-toluene sulfonyl chloride with sodium amalgam, according to the reaction:



Bloomstrand (2) used sodium sulfite in place of the sodium amalgam as a reducing agent for the reduction of the p-toluene sulfonyl chloride. According to Schiller and Otto (3) the sulfinic acids can be easily prepared by adding zinc dust to a cold, alcoholic solution of p-toluene sulfonyl chloride. The zinc salt which is obtained in this method is washed with

(1) Otto, R., Ann., 142, 93 (1867)
(2) Bloomstrand, C:W., Ber., 3, 965 (1870)
(3) Schiller, R. and Otto, R., Ber. 9, 1584-7 (1876)

water and decomposed by sodium carbonate. The solution after having been concentrated was treated with hydrochloric acid in the cold, and the p-toluene sulfinic acid is precipitated. Richter (1) states that the sulfonyl chloride may be dissolved in ether instead of alcohol and then treated with the zinc dust in order to obtain the zinc salt of the sulfinic acid. He also gives a method for producing the sodium salt of the sulfinic acid by the action of thiophenols on benzene sulfonyl chloride as shown by the reaction:

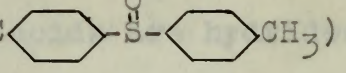
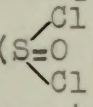


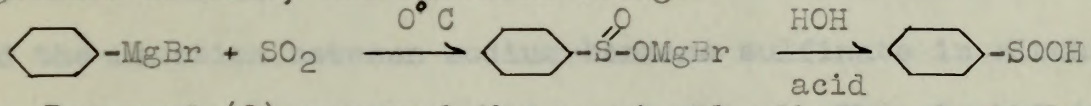
The sodium salt may then be transformed into the sulfinic acid by treatment with hydrochloric acid in the cold.

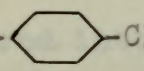
Meister, Lucius and Brüning (2) used sodium sulfide as a reducing agent to reduce the sulfonyl chloride. Fromm and Erfurt (3) prepared the sulfinic acid by the reduction of the sulfonyl chloride with potassium hydrosulfide, and Gutman (4)(5) by the use of sodium arsenite (Na_2AsO_3)as a reducing agent. Knoevenagel and Kenner (6)(7) found that the aromatic sulfinic acids could be prepared readily by the Friedel-Crafts reaction from toluene, aluminum chloride, sulfur dioxide, and hydrochloric acid. They found that an 80% yield was obtained.

---

(1) Richter, V. von., "Organic Chemistry or Chemistry of the Carbon Compounds." Vol. II, p. 179-80. P. Blakiston's Son & Co. (1922)
(2) Meister, Lucius, Brüning, Chem. Zntr. II, 513, (1910)
(3) Fromm, E. and Erfurt, R., Ber. 42, 3821, (1909)
(4) Gutman, A., Ber. 41, 3351, (1908)
(5) Gutman, A., Ber. 42, 480, (1909)
(6) Knoevenagel, E. and Kenner, J., Ber. 41, 3315-22, (1908)
(7) Knoevenagel, E. and Kenner, J., J. Chem. Soc., 83, 7541, (1908)

They also found that the reaction was started by passing hydrogen chloride through the mixture of substances in a suitable reaction container. However sulfoxides () and sulfonium compounds are formed as well as the sulfinic acid. The author states that the aluminum chloride probably adds on to the sulfonyl compound and thus forms the intermediate compound, $AlCl_2.SO_2Cl$. The sulfinic acid can also be made by the Grignard Reaction (1) by passing a stream of sulfur dioxide or adding thionyl chloride () to an ether solution of phenyl magnesium bromide, the reaction being:



Rosamund (2) prepared the previously discussed p-toluene sulfonyl chloride by heating three grams of p-bromo-toluene () for seven hours at 180° C first and then at 200° C with an equivalent amount of sodium sulfite and 15 cubic centimeters of water and one tenth gram of copper sulfate . He filtered the mixture, evaporated and treated it with phosphorus pentachloride and identified the substance as an amide.

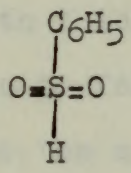
---

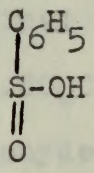
(1) Richter, V. von., "Organic Chemistry or Chemistry of the Carbon Compounds." Vol. II, p. 179-80, P. Blakiston's Son & Co. (1922)

(2) Rosamund, K.W., Ber. 54, 438-40 (1921)

CONSTITUTION AND PROPERTIES OF SULFINIC ACIDS

Otto (1)(2) states that the structure of the sulfinic acids is favored by the hypothesis that the acids are hydrides and do not contain the hydroxyl group, and the sulfur acts as a hexad and not as a tetrad. This is however still open to discussion. To illustrate his view, he uses the formulas shown below:





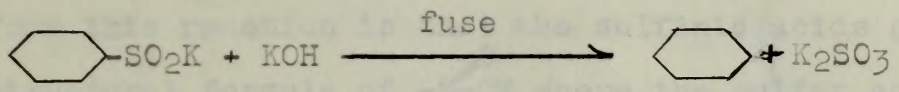
and the reaction between sodium benzene sulfinate in alcoholic solution with alcoholic bromide on warming. The alcohol is distilled off after the reaction is complete and the residue is poured into water. This is a new way of preparing sulfones ( ). The sulfones may also be prepared by the oxidation of ethyl phenyl sulfide ( ) with potassium permanganate in warm glacial acetic acid.

According to Richter (3) and Watts (4) the sulfinic acids are not very stable and are decomposed or broken up into sulfonic acids and disulfoxides, when allowed to stand over concentrated sulfuric acid for a long time, or heated with water. They are also converted into sulfonic acid by air and such oxidizing agents as potassium permanganate and barium peroxide.

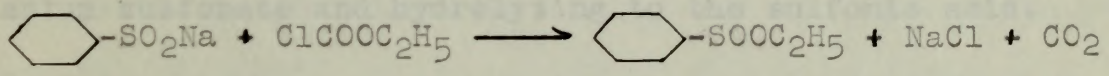
---

(1) Otto, R., Ber. 13, 1272 (1880)
(2) Otto, R., J. Chem. Soc., 38, 810 (1880)
(3) Richter, V. von, "Organic Chemistry or Chemistry of Carbon Compounds." Vol. II, p. 179-80. P. Blakiston's Son & Co. (1922)
(4) Watts, "Dictionary of Chemistry," p. 755-6, Longmans, Green & Co. (1894)

The salts of the sulfinic acids combine with sulfur to form thio-sulfonates, and on reduction with zinc dust they are converted into thio-phenols. If these salts are fused with alkali, they are decomposed into benzenes and alkali sulfites as indicated below:



They react with thionyl chloride to yield sulfinyl chlorides, with aldehydes to form oxysulfones ($H_3C.CH(OH).SO_2C_6H_5$) and they add on to the alpha, beta unsaturated aldehydes, ketones, and carboxylic acids to form sulfones. With acetic anhydride the sulfinic anhydride is formed. With chloro-carbonic esters, they form true sulfinic esters which is shown by the reaction:



Sulfinic acids form slightly soluble ferric salts on reacting with ferric chloride solution.

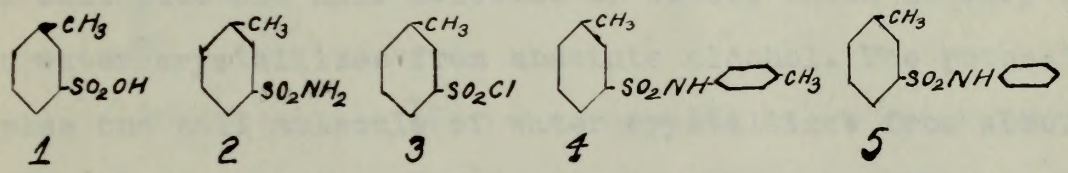
Otto and Rossing (1) have shown that the aromatic sulfinic esters are readily oxidized by potassium permanganate in acetic acid solutions to the corresponding sulfonic esters. For example. 7.8 gm. of ethyl benzene sulfinate dissolved in twenty times its volume of glacial acetic acid and a hot saturated solution of 4.8 gm. of potassium permanganate in 25% acetic acid was added slowly and shaken between additions. The resulting mixture was decolorized by alcohol and diluted with water. It was then extracted with sodium carbonate solution in order to

(1) Otto, R. and Rossing, R., Ber. 19, 1224-7, (1899)

remove the acetic acid. In this way a yellow oil was obtained with the properties of ethyl benzene sulfonate. The esters can be decomposed into potassium benzene sulfonate and alcohol by boiling with aqueous potassium hydroxide solution. The p-toluene sulfonates were also prepared and an interesting fact obtained from this reaction is that the sulfinic acids probably have the structural formula of -S(=O)-OH where the sulfur acts as a tetrad instead of as a hexad as previously stated and as a result conflicts with Otto's original hypothesis. Rossing attributed this fact to the manner in which the alkyl sulfonates are formed. This method also offers a means for preparing the m-toluene sulfonic acid by first preparing the sulfinic ester, oxidizing this to the sulfonic ester, decomposing this to the potassium sulfonate and hydrolyzing to the sulfonic acid.

METHODS OF PREPARING M-TOLUENE SULFONIC ACIDS

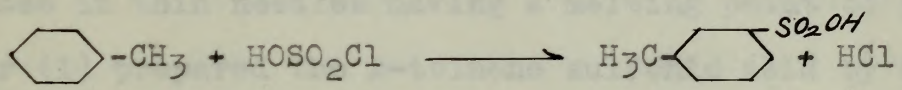
F. H. S. Müller and Wiesinger (1) claim to have prepared m-toluene sulfinic acid and m-toluene sulfonic acid by the action of sulfurous acid on the m-toluene diazonium acid sulfate. The formulas for the free acid, the amide, the chloride, the toluidide and the anilide are given respectively as follows:



1 2 3 4 5

The method for obtaining or isolating the m-toluene sulfonic acid, however, is not stated and this is, of course, what we are interested in.

P. Claissen and Wallen (2) claim to have prepared the m-toluene sulfonic acid by the action of chloro sulfonic acid ($ClSO_3H$) on toluene according to the reaction:



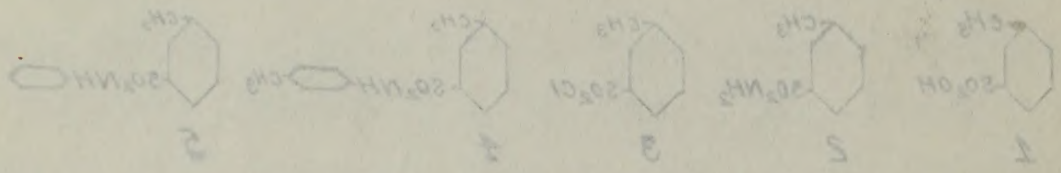
The sulfonyl chlorides crystallize from absolute ether (alcohol and water free) and after heating with water are converted into the acids. A table of the relative properties of these acids is given.

Hubner and Post(3) obtained the m-toluene sulfonic acid by the action of sodium amalgam on a solution of 2-bromo 3-sulfo toluene. The following characteristics of the salts of the m-toluene sulfonic acid were given. The barium salt is very

(1) Müller, F.H. and Wiesinger, F., Ber. 12, 1348-49, (1879)
(2) Claissen, P. and Wallen, P., Ber. 12, 1848 (1879)
(3) Hübner, H. and Post, J., J. Chem. Soc. 27, P. 56-60 (1874)

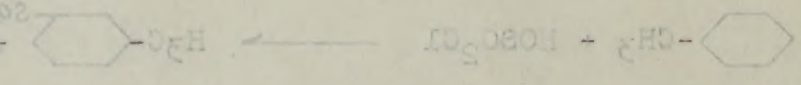
METHODS OF PREPARING M-TOLUENE SULFONIC ACIDS

E. K. S. Muller and Wiesinger (1) claim to have prepared m-toluene sulfonic acid and m-toluene sulfonic acid by the action of sulfuric acid on the m-toluene diazonium acid sulfate. The formulas for the free acid, the amide, the chloride, the toluidid and the sulfide are given respectively as follows:



The method for obtaining or isolating the m-toluene sulfonic acid, however, is not stated and this is, of course, what we are interested in.

P. Claesen and Wallen (2) claim to have prepared the m-toluene sulfonic acid by the action of chloro sulfonic acid ($ClSO_3H$) on toluene according to the reaction:



The sulfonyl chloride crystallizes from absolute ether (alcohol and water free) and after heating with water are converted into the acids. A table of the relative properties of these acids is given.

Huber and Post obtained the m-toluene sulfonic acid by the action of sodium amalgam on a solution of 2-bromo 5-sulfo toluene. The following other derivatives of the salts of the m-toluene sulfonic acid were given. The barium salt is very

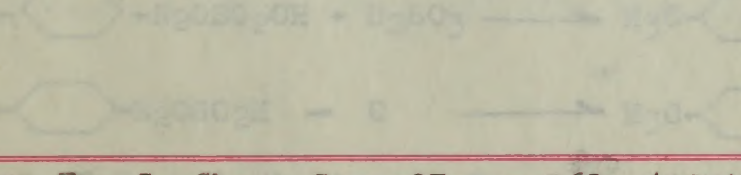
(1) Muller, E.K. and Wiesinger, F., Ber. 12, 1346-49, (1879)
(2) Claesen, P. and Wallen, F., Ber. 12, 1888 (1879)
(3) Huber, H. and Post, J., J. Chem. Soc. 27, K. 56-60 (1874)

soluble in water and alcohol, and forms a crystalline powder. The lead salt crystallizes from a concetrated aqueous solution in thin plates grouped in rosettes, or in long needles from absolute alcohol. The calcium salt is very soluble in water and separates out in small glistening plates when heated in a concentrated alcohol solution and redissolves on cooling. The sodium salt plus one half molecule of water, which is very soluble in water, crystallizes from absolute alcohol. The potassium salt plus one half molecule of water crystallizes from absolute alcohol as large shining plates and resemble naphthalene in appearance.

The m-toluene sulfonyl chloride is a pale yellow liquid which has a very penetrating odor, it does not become a solid at -10° C, and is not decomposed by water at 130° C. Ammonia converts it into the amide which crystallizes from water at 40° C in large plates, and if the water is kept at 20° C, the amide crystallizes in thin needles having a melting point of 90-91° C.

Gewer (1) prepared the m-toluene sulfonic acid by boiling the diazonium salt with absolute alcohol under pressure. He states that the free acid as well as its chloride forms a syrup but the amide crystallizes from hot water and ether in beautiful prisms.

Pechman (2) prepared it from paramido- m-toluene and gives reactions to show this.



(1) Gewer, F., J. Chem. Soc. 27, p. 168 (1874)
(2) Pechman, H. von., J. Chem. Soc. 28, p. 78 (1875)

soluble in water and alcohol, and form a crystalline powder. The lead salt crystallizes from a concentrated aqueous solution in thin pl tes grouped in rosettes, or in long needles from absolute alcohol. The calcium salt is very soluble in water and separates out in small glistening plates when heated in a concentrated alcohol solution and refluxed on cooling. The sodium salt plus one half molecule of water, which is very soluble in water, crystallizes from absolute alcohol. The potassium salt plus one half molecule of water crystallizes from absolute alcohol as large shining plates and resemble naphthalene in appearance.

The p-toluene sulfonyl chloride is a pale yellow liquid which has a very penetrating odor, it does not become a solid at -10° C, and is not decomposed by water at 130° C. Ammonia converts it into the amide which crystallizes from water at 140° in large plates, and if the water is kept at 20° C, the amide crystallizes in thin needles having a melting point of 90-92° C.

Gower (1) prepared the p-toluene sulfonic acid by boiling the diazonium salt with absolute alcohol under pressure. He states that the free acid as well as its chloride form a syrup but the amide crystallizes from hot water and ether in beautiful prisms.

Peckman (2) prepared it from potassio- p-toluene and gives reactions to show this.

(1) Gower, T., J. Chem. Soc. 27, p. 136 (1874)
(2) Peckman, H. von., J. Chem. Soc. 28, p. 78 (1875)

PREPARATION FROM TOLUIDINE ACCORDING TO GATTERMAN'S METHOD

As stated in the introduction, this research is being carried out in order to prepare the m-toluene sulfonic acid from m-toluidine. Although there are no detailed methods described in the literature on the preparation of this acid in this way, it has been stated in several places already mentioned that it has been done. Thus the preparation of the ortho and para sulfonic acids will be discussed.

Muller and Wiesinger (1) as previously mentioned were the first ones to notice the effect of sulfurous acid on diazonium salts, and also Ludwig Gatterman (2) in his article, "Ueber der Ersatz der Diazo Gruppe durch den Sulfinsäurerest." The method described by Gatterman consists in treating 10 gm. p-toluidine with 25 cc. conc. sulfuric acid and 15 gm. water in order to form the p-toluidine acid sulfate, (H_3C-C$_6$H$_4$-NH_3OSO_2OH). The solution is then cooled to 0° C and then 8 gm. sodium nitrite dissolved in 40 gm. water are added to the toluidine salt while cold, and produces the p-toluene diazonium acid sulfate. This solution is then saturated with sulfur dioxide in the cold and 10 gm. dry copper powder are added. The reactions which take place are as follows, in this order:

1). H_3C-C$_6$H$_4$-NH_2 + $HOSO_2OH$ ⟶ H_3C-C$_6$H$_4$-NH_3OSO_2OH

2). H_3C-C$_6$H$_4$-NH_3OSO_2OH + HONO ⟶ H_3C-C$_6$H$_4$-N_2OSO_2OH

3). H_3C-C$_6$H$_4$-N_2OSO_2OH + H_2SO_3 ⟶ H_3C-C$_6$H$_4$-N_2OSO_2H

4). H_3C-C$_6$H$_4$-N_2OSO_2H − O ⟶ H_3C-C$_6$H$_4$-N_2SO_2H

(1) Müller, F.H. and Wiesinger, F., Ber. 12, 1348 (1879)
(2) Gatterman, L., Ber. 32, 1136 (1899)

PREPARATION FROM TOLUIDINE ACCORDING TO BATTERMAN'S METHOD

As stated in the introduction, this reaction is being carried out in order to prepare the p-toluene sulfonic acid from p-toluidine. Although there are no detailed methods described in the literature on the preparation of this acid in this way, it has been stated in several places already mentioned that it had been done. Thus the preparation of the ortho and para sulfonic acids will be discussed.

Muller and Wieninger (1) as previously mentioned were the first ones to notice the effect of sulfurous acid on diazonium salts, and also Ludwig Batterman (2) in his article, "Ueber der Einwirk der Diazo Gruppe durch den Sulfinsäurerest." The method described by Batterman consists in treating 10 gm. p-toluidine with 25 cc. conc. sulfuric acid and 15 gm. water in order to form the p-toluidine acid sulfate, ($H_3C-C_6H_4-NH_3OSO_2OH$). The solution is then cooled to 0°C and then 8 gm. sodium nitrite dissolved in 40 gm. water are added to the toluidine salt while cold, and produces the p-toluene diazonium acid sulfate. This solution is then saturated with sulfur dioxide in the cold and 10 gm. dry copper powder are added. The reactions which take place are as follows, in this order:

1). $H_3C-C_6H_4-NH_3 + HOSO_2OH \longrightarrow H_3C-C_6H_4-NH_3OSO_2OH$

2). $H_3C-C_6H_4-NH_3OSO_2OH + NO_2O \longrightarrow H_3C-C_6H_4-N_2OSO_2OH$

3). $H_3C-C_6H_4-N_2OSO_2OH + H_2SO_3 \longrightarrow H_3C-C_6H_4-N_2OSO_2H$

4). $H_3C-C_6H_4-N_2OSO_2H + O \longrightarrow H_3C-C_6H_4-N_2SO_3H$

(1) Muller, F.H. und Wieninger, K., Ber. 72, 1948 (1939)
(2) Batterman, L., Ber. 32, 1136 (1899)

5). $H_3C-C_6H_4-N_2SO_2H - N_2 \xrightarrow[\text{powder}]{Cu} H_3C-C_6H_4-SO_2H + N_2$

Thus as Gatterman shows there are two possibilities that the oxygen may be taken away, either by the finely divided copper powder or by the sulfur dioxide.

In an English patent of 1896, communicated from abroad, the manufacture or production of sulfinic acids of the aromatic series is described. This is analagous to that published by Gatterman, but gives a clearer discussion of the probable mechanism of the reactions which take place. The equations are:

1). $C_6H_5-N_2OSO_2OH + H_2SO_3 \longrightarrow C_6H_5-N_2SO_2OH + H_2SO_4$

2). $2\ C_6H_5-N_2SO_2OH + H_2SO_3 \text{ or Cu} \longrightarrow 2\ C_6H_5-SO_2H + 2N_2 + H_2SO_4 \text{ or CuO}$

This also designates that the one molecular proportion of oxygen is taken away either by the action of H_2SO_3 or copper and one molecular proportion of nitrogen is eliminated by the action of the copper on the diazonium sulfite. It is also emphasized that the reaction will proceed in a similar manner if other diazonium salts are used in the place of the diazonium sulfate in equation 1.

Gatterman extracted the p-toluene sulfinic acid with ether from the solution and sludge which were obtained from the reaction. The ether solution was then treated with a sodium carbonate solution in order to separate the sulfinic acid as its sodium salt, which is very soluble in a water solution. The water layer is then drawn off from the ether layer and is

3). H_2O-⬡-NSO_2H - N_2 —(Cu powder)→ H_2-⬡-SO_2H + N_2

Thus as Gattermann shows there are two possibilities that the oxygen may be taken away, either by the finely divided copper powder or by the sulfur dioxide.

In an English patent of 1896, communicated from abroad, the manufacture or production of sulfinic acids of the aromatic series is described. This is analogous to that published by Gattermann, but gives a clearer discussion of the probable mechanism of the reactions which take place. The equations are:

1). ⬡-NSO_2OH + H_2SO_3 ——→ ⬡-NSO_2Cl + H_2SO_4

2). 2 ⬡-NSO_2OH + H_2SO_3 —(or Cu)→ 2 ⬡-SO_2H + $2N_2$ + H_2SO_4

This also designates that the one molecular proportion of oxygen is taken away either by the action of H_2SO_3 or copper and one molecular proportion of nitrogen is eliminated by the action of the copper on the diazonium sulfite. It is also emphasized that the reaction will proceed in a similar manner if other diazonium salts are used in the place of the diazonium sulfate in equation 1.

Gattermann extracted the p-toluene sulfinic acid with ether from the solution and sludge which were obtained from the reaction. The ether solution was then treated with a sodium carbonate solution in order to separate the sulfinic acid as its sodium salt, which is very soluble in a water solution. The water layer is then drawn off from the ether layer and is

treated with concentrated hydrochloric acid in the cold which precipitates the solid sulfinic acid from the solution. Gatterman obtained an eighty percent yield by this method.

The following preparation of benzene sulfinic acid is quoted from the patent (1). "One part of aniline is dissolved in a mixture prepared from three parts of concentrated sulfuric acid and 15 parts of water, and diazotized in the usual manner. The diazo solution thus obtained is quickly introduced, with energetic stirring and careful cooling into an excess of a saturated water solution of sulfurous anhydride, to which six parts of copper powder have been added. A rapid development of nitrogen takes place, and the reaction is finished when the development of nitrogen ceases and the diazo compound is no longer found in the reaction mixture. The sulfinic acid thus produced can easily be isolated by extracting the mixture with ether, and evaporating the ethereal solution. It exhibits the properties of the known benzene sulfinic acid, m.p. 83-84° C."

On further search through the literature, an improved method was given by John Thomas (2) who states that the primary aromatic amino compounds can be converted into their corresponding sulfinic acids with practically quantitative yields by the Gatterman method and therefore offers a very satisfactory method for replacing the amino radical by the sulfinic radical. He also states that the sulfinic acid has been generally obtained by extraction with ether, but this part of the operation is not the best or very convenient for prepara-

(1) E.P. 26139 of 1896.
(2) Thomas, J., J. Chem. Soc. p. 344 (1909)

tion on a large laboratory scale.

Working on the suggestion of W.J. Pope which was to try to precipitate the sulfinic acids as iron salts, he found that they all precipitated as ferric salts, quantitatively from a strongly acid solution on adding ferric chloride. The ferric salts were orange precipitates, which are fairly stable in dry air and as a result can be easily filtered and washed. Thus Thomas concluded that the sulfinic acids are characterized by this property of yielding yellow to orange ferric salts which are insoluble in water and strongly acid solution. The free sulfinic acids are obtained from the ferric salts by treatment with alkalies, which precipitate the iron as ferric hydroxide and the sulfinic acid remains in solution of the alkali as an alkali salt, from which the free acid is precipitated by adding concentrated hydrochloric acid in the cold.

The procedure in outline form may be divided into five parts: (a) filtering solution obtained from preparation of sulfinic acid and washing the residue with dilute ammonia; (b) allowing the ammoniacal washings to mix with sulfuric acid filtrate; (c) adding concentrated ferric chloride solution to the solution which still contains an excess of sulfuric acid until no further precipitate falls; (d) filtering the bright orange yellow precipitate and washing the ferric salt with water and drying with the aid of a little alcohol; (e) and treating the ferric p-toluene sulfinate with a slight excess of aqueous ammonia, filtering from the ferric hydroxide and acidifying with

concentrated hydrochloric acid in the cold so that the sulfinic acid will separate out as a mixture of sulfinic acid with its anhydride, which yields the acid as a pure white product with a melting point from 86-87° C on recrystallization from water. By this method Thomas obtained 12.5 gm. of ferric p-toluene sulfinate from 10 grams of p-toluidine. Thomas also describes how to make the sulfonyl chloride by treating a solution of the sulfinic acid in sodium carbonate with sodium hypochlorite, and the sulfonamide by decomposing the ferric salt with ammonia and then treating it with sodium hypochlorite. This method is also described and covered by the English patents, numbers 3055 and 13056 of 1906.

IMPROVED METHODS

It has been shown that copper sulfate may be used instead of copper powder in preparing the sulfinic acids by the Gatterman method accoring to the English patent number 13054 of 1906. The fact is brought out that cuprous oxide, cuprous hydroxide, cuprous sulfite or ethyl alcohol, together with the cupric oxide, cupric hydroxide or other cupric compounds may be used in place of the copper powder in the Gatterman method. Cuprous sulfide is also (1) used in place of the finely divided copper powder of the Gatterman method. It was found that if cuprous sulfide or a compound containing it was used, a considerable improvement in the method is effected since the cuprous sulfide can be prepared more cheaply and easily than the finely divided copper powder and other copper compounds.

(1) E.P. 7288 of 1906.

The method for the preparation of o-toluene sulfinic acid (1) is as quoted below. "Twenty parts of o-toluidine (dissolved in a mixture of sixty parts of ordinary concentrated sulfuric acid and two hundred parts of water) are diazotized by means of sodium nitrite in the usual manner. Sulfur dioxide is passed into the solution until it is saturated and subsequently five parts of cuprous sulfide, finely divided and in a moist condition are added little by little, the passage of sulfur dioxide continued until the evolution of nitrogen has entirely ceased. Throughout the process the temperature should not be allowed to rise above 5° C. When the evolution of nitrogen ceases, the solution is filtered and extracted with ether. On evaporation of the ethereal solution, the o-toluene sulfinic acid is obtained in a dry state."

Cain (2) described a method by which cuprous oxide is used for the decomposition of the diazonium salt. Nine and three tenths kilos of aniline are dissolved in 150 kilos of 20% sulfuric acid and diazotized. Sulfur dioxide is passed into the solution (15 kilos) and 15 kilos of cuprous oxide are added with stirring to the solution which is kept below 5° C. The cuprous oxide is added a little at a time to insure the reaction being completed.

A very interesting article is that describing the use of cuprous oxide which eliminates the extraction with ether or precipitating the sulfinic acid as the ferric salts. The sulfinic acid is also prepared according to this method, more

(1)E.P. 7288 of 1906.
(2) Cain, J.C., "The Chemistry and Technology of the Diazo-Compounds," p. 65, Edward Arnold. (1920)

quickly and completely by diazotizing the amine using hydrochloric acid instead of the sulphuric acid. The procedure (1) for preparing the benzene sulfinic acid is quoted below. "9.3 parts of aniline dissolved in 40 parts of HCl of 20% strength are diazotized with 7 parts of $NaNO_2$ in 10 parts of water, at a temperature of 0° to 5° C. To this diazo solution, are added while stirring, 30 parts of a solution of sodium bisulfite of 40 % strength, then 40 parts of alcoholic sulphurous acid of 35% strength, at a temperature between 0-5° C, and finally a concentrated aqueous solution of 2.5 parts of copper sulfate, that is a quantity corresponding with 5% of the theoretical proportion of cuprous oxide. While stirring vigorously, the temperature is gradually raised to 15° C. When the evolution of nitrogen is finished, the solution is neutralized with soda, the alcohol distilled from it and the cool filtered solution is acidified with HCl, the sulfinic acid which separates out is filtered and purified by dissolution in soda and reprecipitation with HCl."

(1) E.P. 12871 of 1900.

EXPERIMENTAL

P-toluene sulfinic acid was prepared according to the method outlined by Gatterman (1). The p-toluene sulfinic acid was prepared in order to perfect the technique and because of the cost of the m-toluidine. One mole weight of the p-toluidine which is a white lustrous organic compound with a melting point of 45°C was used. The p-toluidine is insoluble in cold water but dissolves in a concentrated sulfuric acid solution forming the p-toluidine sulfate. The quantities necessary to diazotize the reaction were calculated from the equations:

1). $H_3C-C_6H_4-NH_2 + HOSO_2OH \longrightarrow H_3C-C_6H_4-NH_3OSO_2OH$

2). $NaNO_2 + HOSO_2OH \longrightarrow NaHSO_4 + HONO$

3). $H_3C-C_6H_4-NH_3OSO_2OH + HONO \xrightarrow{or} H_3C-C_6H_4-N_2OSO_2OH + 2\,H_2O$

Thus 107 gm. of p-toluidine were dissolved in 250 gm. of sulfuric acid and 1500 gm. of water, the excess sulfuric acid being added in order to react with the $NaNO_2$ and furnish the nitrous acid which is needed in the operation of diazotizing the p-toluidine to the p-toluidine diazonium sulfate.

APPARATUS

The apparatus used in the preparation is as illustrated by Figure (1) and consists of: (a) the reaction flask; (b) the cooling tank; (c) the separatory funnel for the addition of the sodium nitrite solution; (d) the sulfur dioxide tank; (e) sulfur dioxide inlet; (f) inlet for copper powder; (g) outlet tube for separatory funnel as described below; (h) gas trap for absorbing excess sulfur dioxide; (i) mechanical stirrer.

(1) Gatterman, L., Ber. 32, 1136 (1899)

EXPERIMENTAL

p-toluene sulfinic acid was prepared according to the method outlined by Datterman (1). The p-toluene sulfinic acid was prepared in order to perfect the technique and because of the cost of the p-toluidine. One mole weight of the p-toluidine which is a white lustrous organic compound with a melting point of 45°C was used. The p-toluidine is insoluble in cold water but dissolves in a concentrated sulfuric acid solution forming the p-toluidine sulfate. The quantities necessary to dissolve the reaction were calculated from the equations:

1). $H_3C-C_6H_4-NH_2 + HOSO_2CH \longrightarrow H_3C-C_6H_4-NH_2OSO_2CH$

2). $NaNO_2 + HOSO_2CH \longrightarrow NaHSO_4 + HONO$

3). $H_3C-C_6H_4-NH_2OSO_2OH + HONO \xrightarrow{CH_3} H_3C-C_6H_4-N_2OSO_2OH + 2\,H_2O$

Thus 107 gm. of p-toluidine were dissolved in 250 gm. of sulfuric acid and 1500 gm. of water, the excess sulfuric acid being added in order to react with the $NaNO_2$ and furnish the nitrous acid which is needed in the operation of dissolving the p-toluidine to the p-toluidine diazonium sulfate.

APPARATUS

The apparatus used in the preparation is as illustrated by Figure (1) and consists of: (a) the reaction flask; (b) the cooling tank; (c) the separatory funnel for the addition of sodium nitrite solution; (d) the sulfur dioxide tank; (e) sulfur dioxide inlet; (f) inlet for copper powder; (g) outlet tube for separatory funnel as described below; (h) gas trap for absorbing excess sulfur dioxide; (i) magnetical stirrer.

(1) Datterman, L., Ber., 32, 1136 (1899)

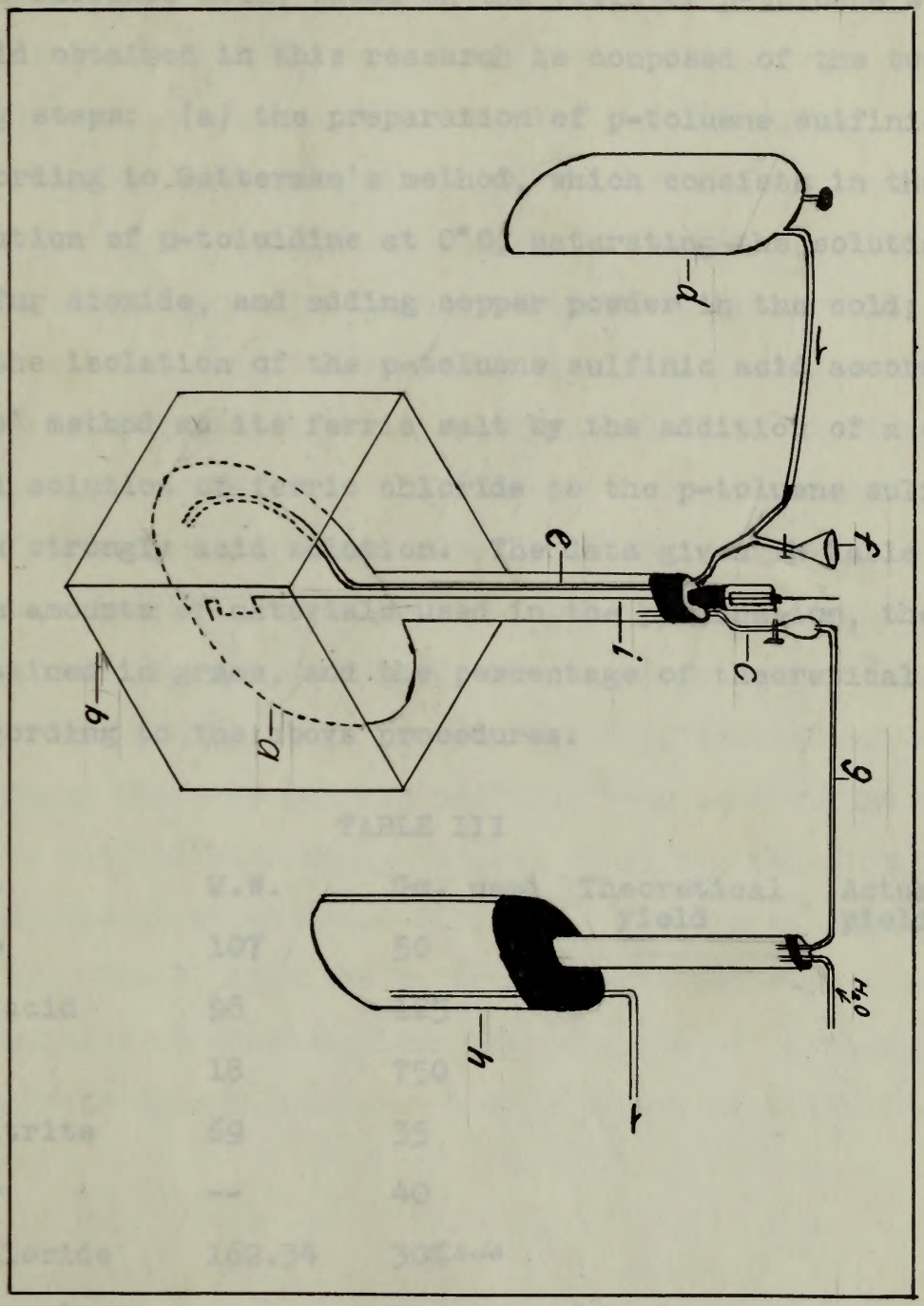


Figure 1.

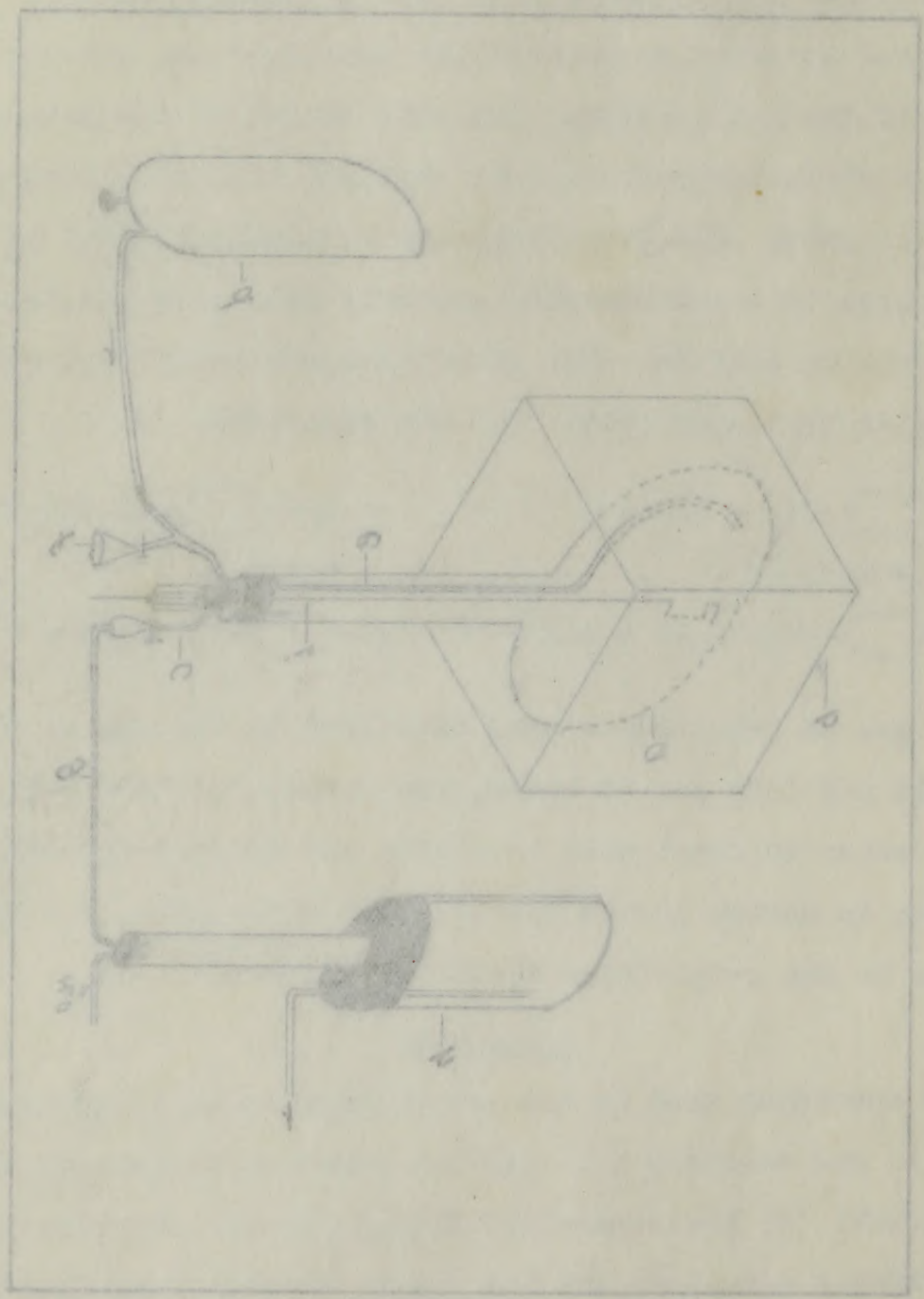


Figura 1

PROCEDURE

The best single specific procedure for the preparation of p-tolyene sulfinic acid, based on the yield of p-toluene sulfinic acid obtained in this research is composed of the two following steps: (a) the preparation of p-toluene sulfinic acid according to Gatterman's method, which consists in the diazotization of p-toluidine at 0° C, saturating the solution with sulfur dioxide, and adding copper powder in the cold; (b) and the isolation of the p-toluene sulfinic acid according to Thomas' method as its ferric salt by the addition of a concentrated solution of ferric chloride to the p-toluene sulfinic acid in a strongly acid solution. The data given in Table III shows the amounts of materials used in the preparation, the yield obtained in grams, and the percentage of theoretical yield according to the above procedures.

TABLE III

Substance	M.W.	Gm. used	Theoretical yield	Actual yield
toluidine	107	50		
sulfuric acid	98	125		
water	18	750		
sodium nitrite	69	35		
Cu powder	--	40		
ferric chloride	162.34	30% Soln.		
p-toluene sulfinic acid M.P. 85-86° C.			72.80 gm.	15 gm. 20.60% (of theoretical)

PROCEDURE

The best single specific procedure for the preparation of p-toluene sulfinic acid, based on the yield of p-toluene sulfinic acid obtained in this research is composed of the two following steps: (a) the preparation of p-toluene sulfinic acid according to Gattermann's method, which consists in the diazotization of p-toluidine at 0°C, saturating the solution with sulfur dioxide, and adding copper powder in the cold; (b) and the isolation of the p-toluene sulfinic acid according to Thomas' method as its ferric salt by the addition of a concentrated solution of ferric chloride to the p-toluene sulfinic acid in a strongly acid solution. The data given in Table III shows the amounts of materials used in the preparation, the yield obtained in grams, and the percentage of theoretical yield according to the above procedure.

TABLE III

Substance	M.W.	Gm. used	Theoretical Yield	Actual Yield
toluidine	107	50		
sulfuric acid	98	125		
water	18	750		
sodium nitrite	69	35		
Cu powder	--	40		
ferric chloride	162.34	50% soln.		
p-toluene sulfinic acid M.P. 83-86°C.			72.80 Gm. (of theoretical)	15 Gm. 20.60%

The p-toluidine, sulfuric acid and water solution are placed in the reaction flask (a) and the solution is cooled to 0°C by means of an ice-salt mixture in the cooling tank (b). The mechanical stirrer (h) keeps the p-toluidine in the form of a finely divided substance which settles out in cooling. When the temperature has reached 0°C, the sodium nitrite solution is added to the separatory funnel (c) and the solution is diazotized according to the method outlined by Gatterman (1). The sodium nitrite solution is added slowly to the cooled solution which is well stirred by the mechanical stirrer. The addition of the sodium nitrite solution is continued until three fourths of the nitrite solution has been added, then it is tested with starch potassium iodide paper. A drop of the solution is allowed to drop on a piece of starch potassium iodide paper. If dark spots don't appear on the starch potassium iodide paper it means that the nitrous acid has been used up and then more sodium nitrite solution is added, until the reaction is almost complete at which point very small amounts of the nitrite solution are added. When the solution in the reaction flask, after standing 5-10 minutes shows the presence of nitrous acid by testing with starch potassium iodide paper, diazotization is complete.

(1) Gatterman, L., "Practical Methods of Organic Chemistry," p. 240-1, Macmillan Co. (1914)

The p-toluidine, sulfuric acid and water solution are placed in the reaction flask (a) and the solution is cooled to 0°C by means of an ice-salt mixture in the cooling tank (b). The mechanical stirrer (M) keeps the p-toluidine in the form of a finely divided substance which settles out in cooling. When the temperature has reached 0°C, the sodium nitrite solution is added to the separatory funnel (c) and the solution is discontinued according to the method outlined by Batterman (1). The sodium nitrite solution is added slowly to the cooled solution which is well stirred by the mechanical stirrer. The addition of the sodium nitrite solution is continued until three fourths of the nitrite solution has been added, then it is tested with starch potassium iodide paper. A drop of the solution is allowed to drop on a piece of starch potassium iodide paper. If dark spots don't appear on the starch potassium iodide paper it means that the nitrous acid has been used up and then more sodium nitrite solution is added, until the reaction is almost complete at which point very small amounts of the nitrite solution are added. When the solution in the reaction flask, after standing 5-10 min.too shows the presence of nitrous acid by testing with starch potassium iodide paper, diazotization is complete.

(1) Batterman, L., "Practical Methods of Organic Chemistry," p. 240-1, Macmillan Co. (1914)

ADDITION OF SULFUR DIOXIDE

Next the outlet tube for the excess gases is substituted for the separatory funnel and all the connections are made air tight by sealing with melted paraffin. The sulfur dioxide tank is then opened and sulfur dioxide passed into the solution until the solution has become saturated with the gas. Care must be taken that the reaction mixture temperature shall not rise above 4°C. After the solution has become saturated, 70 gm. of dry copper powder is added slowly while stirring and continuing to pass in the sulfur dioxide. The sulfur dioxide addition is continued for one half hour after the last portion of copper powder has been added. The reaction mixture is allowed to stand for a while until the greatest portion of the sulfur dioxide has gone over into the absorption trap.

The solution and solid matter are then extracted twice with about one liter of ether solution each time in order to extract the sulfinic acid formed. The color of the solution from the reaction vessel before the extraction was a light green showing the probability of the formation of cupric sulfate. The ether solution was dark colored due to impurities extracted with the sulfinic acid. In order to decrease the working volume about one liter of ether was distilled off and the remainder was extracted with an equivalent amount by weight of sodium hydroxide made up into a 20% solution to extract the sulfinic acid as its sodium salt which is soluble in water. The water extract is then treated with concentrated HCl and a yel-

ADDITION OF SULFUR DIOXIDE

Next the outlet tube for the excess gases is substituted for the separatory funnel and all the connections are made air tight by sealing with melted paraffin. The sulfur dioxide tank is then opened and sulfur dioxide passed into the solution until the solution has become saturated with the gas. Care must be taken that the reaction mixture temperature shall not rise above 4°C. After the solution has become saturated, 70 gm. of dry copper powder is added slowly while stirring and continuing to pass in the sulfur dioxide. The sulfur dioxide addition is continued for one half hour after the last portion of copper powder has been added. The reaction mixture is allowed to stand for a while until the greatest portion of the sulfur dioxide has gone over into the absorption trap.

The solution and solid matter are then extracted twice with about one liter of ether solution each time in order to extract the sulfinic acid formed. The color of the solution from the reaction vessel before the extraction was a light green showing the probability of the formation of cupric sulfate. The ether solution was dark colored due to impurities extracted with the sulfinic acid. In order to decrease the working volume about one liter of ether was distilled off and the remainder was extracted with an equivalent amount by weight of sodium hydroxide made up into a 20% solution to extract the sulfinic acid as its sodium salt which is soluble in water. The water extract is then treated with concentrated HCl and a yel-

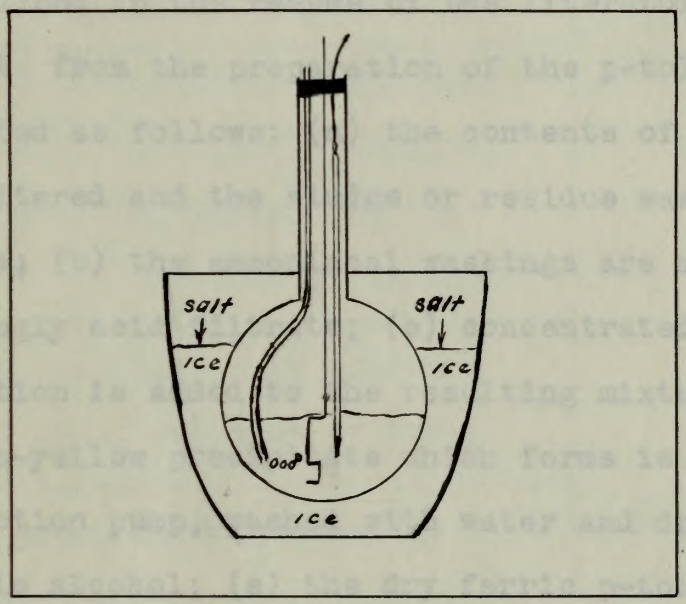
lowish precipitate of the sulfinic acid is obtained. The quantity was small however, due to losses encountered in the several extraction processes. Twelve grams of the pure acid were obtained which had a melting point of 85°C.

The causes for the small yield may be summed up as follows: (a) incomplete diazotization; (b) temperature of the reaction too high; (c) copper powder added too rapidly; (d) the difficulties involved in extracting and purifying the acid and also the possibility of side reactions because of the larger quantity used.

ISOLATION OF P-TOLUENE SULFINIC ACID AS THE IRON SALT

With these factors in mind, it was decided to make a run using only 50 grams of the p-toluidine and to employ the method of precipitating the sulfinic acid as its ferric salt from a strongly acid solution as suggested by Thomas. The procedure is carried out as outlined on page 19. The method of cooling the reaction mixture was also slightly changed. A metal container is set up as in Figure 3, the reaction flask is set on a support in cracked ice up to the point indicated in the diagram. Salt is placed on top of the ice, and this salt diffusing through the ice will cool the contents of the flask to 0°C. It was found that the temperature of the mixture could be kept below 0°C by this method, by inserting a thermometer from time to time and reading the temperature. It was also found that it was advisable to add a few small pieces of cracked ice to the reaction mixture to insure the maintainance of 0°C

Figure 2.

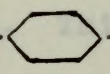


temperature and to prevent too rapid rise of temperature due to the diazotization reaction. With the exception of the change in the cooling mechanism, the procedure for the preparation of the sulfinic acid was carried out as before and the difference comes in the isolation of the sulfinic acid.

The p-toluene sulfinic acid is isolated first as its ferric salt and then converted into the free acid according to the procedure outlined in the resume of the literature. The reaction product from the preparation of the p-toluene sulfinic acid was treated as follows: (a) the contents of the reaction vessel was filtered and the sludge or residue was washed with dilute ammonia; (b) the ammoniacal washings are mixed with the original strongly acid filtrate; (c) concentrated ferric chloride solution is added to the resulting mixture from (b); (d) the orange-yellow precipitate which forms is filtered by use of the suction pump, washed with water and dried with the aid of a little alcohol; (e) the dry ferric p-toluene sulfinate is treated with a slight excess of aqueous ammonia, the ferric hydroxide is removed by filtration and the resulting solution is neutralized with concentrated hydrochloric acid in the cold in order to precipitate the sulfinic acid as a mixture of the sulfinic acid and its anhydride; (f) the precipitate from (e) is filtered and recrystallized from hot water in order to obtain the free acid pure; (g) and lastly the melting point is determined. If the acid does not melt at the correct melting point it must be recrystallized again from hot water. Noyes'

system of tabulation (1) found in Table IV will serve to illustrate how the precedure was carried out and what happened.

TABLE IV.

<table>
<tr><td colspan="3">Reaction Mixture: Filter</td></tr>
<tr><td colspan="2"><u>Residue</u>
Copper sludge and sulfinic acid.
Wash with dilute ammonia.</td><td><u>Filtrate</u>
Green solution.</td></tr>
<tr><td><u>Residue</u>
Copper and other insoluble matter.</td><td>Light blue solution of H_3C-  -SO_2NH_4 in water. Add to original filtrate.</td><td rowspan="5"></td></tr>
<tr><td colspan="2">Greenish white precipitate in presence of H_2SO_4. Add conc. solution of $FeCl_3$.</td></tr>
<tr><td colspan="2">Orange yellow precipitate. Dried on filter and washed with water.</td></tr>
<tr><td colspan="2">Treat with slight excess NH_4OH.</td></tr>
<tr><td rowspan="2"><u>Residue.</u>
$Fe(OH)_3$</td><td>Solution of sulfinic acid salt. Treat with conc. HCl in cold.</td></tr>
<tr><td>White precipitate recrystallizes from hot water as pure white crystals, m.p. 85-86°C.</td><td></td></tr>
</table>

(1) Noyes, A.A., "Qualitative Chemical Analysis," p. 60, Macmillan Co. (1920)

system of tabulation (1) found in Table IV will serve to illustrate how the procedure was carried out and what happened.

TABLE IV.

Reaction Mixture: Filter	
Residue Copper sludge and sulfinic acid. Wash with dilute ammonia.	Filtrate Green solution.
Residue Copper and other insoluble matter.	Light blue solution of $H_3O\text{-}\langle\bigcirc\rangle\text{-}SO_2^-NH_4^+$ in water. Add to original filtrate.
Greenish white precipitate in presence of H_2SO_4. Add conc. solution of $FeCl_3$.	
Orange yellow precipitate. Dried on filter and washed with water.	
Treat with slight excess NH_4OH.	
Residue. $Fe(OH)_3$	Solution of sulfinic acid salt. Treat with conc. HCl in cold.
	White precipitate readily crystallizes from hot water as pure white crystals, m.p. 85-86°C.

(1) Noyes, A.A., "Qualitative Chemical Analysis," p. 60, Macmillan Co. (1920)

OBSERVATIONS

The following facts were noted in carrying out the above procedure:

(a) On filtering the mixture in the reaction flask, a clear light blue solution was obtained and a brownish copper sludge remained on the filter paper.

(b) On washing the copper sludge with dilute ammonium hydroxide a yellow precipitate settled out in the bottom of the filter flask which dissolved on the addition of more dilute ammonium hydroxide solution. This can be attributed to the fact that the sulfinic acid itself is insoluble in cold water while its salts such as the sodium or ammonium are very soluble in cold water. The excess ammonium hydroxide that was added formed ammonium sulfinate which was soluble.

(c) A greenish white precipitate was formed when the alkaline solution was added to the original acid filtrate. This was probably due to the conversion of the ammonium salt into the sulfinic acid by the excess sulfuric acid in the mixture.

(d) When concentrated ferric chloride was added to the reaction products of (c), an orange yellow precipitate was formed which was ferric p-toluene sulfinate which showed that the original greenish white crystals which formed on the addition of the ammonium hydroxide solution to the original acid filtrate solution was the sulfinic acid which finally was converted into the ferric salt. The light green color was probably due to the adsorption of some of the copper sulfate solution

OBSERVATIONS

The following facts were noted in carrying out the above procedure:

(a) On filtering the mixture in the reaction flask, a clear light blue solution was obtained and a brownish copper sludge remained on the filter paper.

(b) On washing the copper sludge with dilute ammonium hydroxide a yellow precipitate settled out in the bottom of the filter flask which dissolved on the addition of more dilute ammonium hydroxide solution. This can be attributed to the fact that the sulfinic acid ibsalt is insoluble in cold water while its salts such as the sodium or ammonium are very soluble in cold water. The excess ammonium hydroxide that was added formed ammonium sulfinate which was soluble.

(c) A greenish white precipitate was formed when the alkaline solution was added to the original acid filtrate. This was probably due to the conversion of the ammonium salt into the sulfinic acid by the excess sulfuric acid in the mixture.

(d) When concentrated ferric chloride was added to the reaction products of (c), an orange yellow precipitate was formed which was ferric p-toluene sulfinate which showed that the original greenish white crystals which formed on the addition of the ammonium hydroxide solution to the original acid filtrate solution was the sulfinic acid which finally was converted into the ferric salt. The light green color was probably due to the adsorption of some of the copper sulfate solution

formed in the original reaction flask.

(e) Thus it was concluded that the formation of all precipitates on the addition of the ammonium hydroxide extract to the green acid solution should be disregarded and the ferric chloride solutions should be added directly to the mixture of the ammonium hydroxide extract and the green acid solution obtained by filtering the original mixture.

(f) On recrystallization from hot water the sulfinic acid obtained was perfectly white and had a melting point of 85-86 °C.

On carrying out the procedure for the isolation of the p-toluene sulfinic acid as its ferric salt in another run, the following facts were noted:

(a) An orange yellow precipitate was obtained when concentrated ferric chloride solution was added to the mixture of the aqueous ammonium hydroxide extract and the original green acid filtrate.

(b) On allowing this precipitated iron salt to stand in the acid solution for 12 hours the orange color disappeared and in its place there remained a light yellow precipitate. It was assumed that the ferric salt in some manner had been converted into the sulfinic acid again and that the ferric chloride had been converted into ferrous sulfate during which the ferric chloride acted as an oxidising agent and converted some of the sulfinic acid into sulfonic acid which was soluble in the solution.

formed in the original reaction flask.

(e) Thus it was concluded that the formation of all precipitates on the addition of the ammonium hydroxide extract to the green acid solution should be disregarded and the ferric chloride solutions should be added directly to the mixture of the ammonium hydroxide extract and the green acid solution obtained by filtering the original mixture.

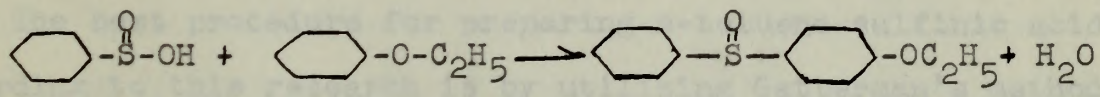
(f) On recrystallization from hot water the sulfinic acid obtained was perfectly white and had a melting point of 85-86 °C.

On carrying out the procedure for the isolation of the p-toluene sulfinic acid as its ferric salt in another run, the following facts were noted:

(a) An orange yellow precipitate was obtained when concentrated ferric chloride solution was added to the mixture of the aqueous ammonium hydroxide extract and the original green acid filtrate.

(b) On allowing this precipitated iron salt to stand in the acid solution for 12 hours the orange color disappeared and in its place there remained a light yellow precipitate. It was assumed that the ferric salt in some manner had been converted into the sulfinic acid again and that the ferric chloride had been converted into ferrous sulfate during which the ferric chloride acted as an oxidizing agent and converted some of the sulfinic acid into sulfonic acid which was soluble in the solution.

(c) To ascertain the validity of the above assumption, the mixture obtained in (b) was filtered and the precipitate dried by pressing between two wooden blocks padded with filter paper. One portion of the green solution was treated with potassium ferricyanide in order to test for the presence of the ferrous ion. A blue precipitate was obtained which is a positive test for the ferrous ion. A second portion of the green solution was treated with potassium thiocyanate and a red color and a white precipitate resulted giving positive indications of the presence of the ferric ion. These tests showed that the original assumption made was correct and it was concluded that the ferric salt must be filtered immediately after precipitation in order to prevent the above from taking place. The light yellow precipitate obtained was recrystallized from hot water, furnishing a crystalline substance which melted between 85-86°C. This was also tested according to "Smiles" test (1) for the presence of sulfinic acid and a positive test was obtained. The equation for this test is:



On dissolving the aromatic sulfinic acid in concentrated H_2SO_4 and adding a drop of anisol, a blue color was obtained which is due to the formation of a para sulbstituted aromatic sulfoxide by elimination of water.

(1) Clark, H.T., "A Handbook of Organic Analysis," p. 57, Edward Arnold & Co. (1931)

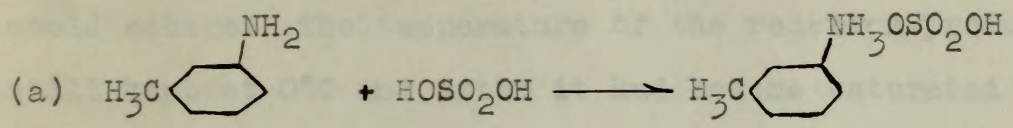
PREPARATION OF META-TOLUENE SULFINIC ACID

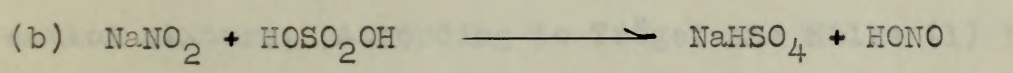
Meta toluene sulfinic acid was prepared from m-toluidine according to Gatterman's method in the same way as the p-toluene sulfinic acid. The procedure already described under the preparation of the p-toluene sulfinic acid was followed very closely and special care was taken to overcome the difficulties noted under that preparation. In the preparation of the meta-toluene sulfinic acid 10 gram portions of the m-toluidine were used instead of 50 or 100 gram portions as in the preparation of the p-toluene sulfinic acid. The apparatus was also altered slightly in order to be able to note the different stages of the reaction, i.e. a glass battery jar was substituted for the metal container used as a cooling medium in the preparation of the p-toluene sulfinic acid. The reaction vessel was also changed from a one mouthed flask to a three mouthed flask. The contents of the reaction vessel were cooled as illustrated by figure 2 and the temperature was kept at 0°C throughout the entire process.

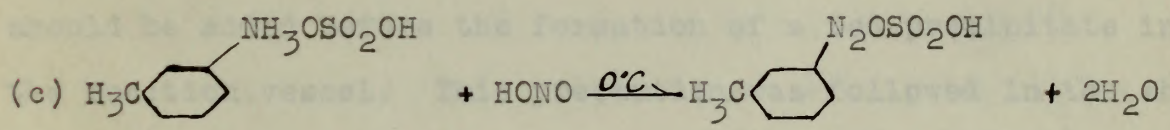
The best procedure for preparing m-toluene sulfinic acid according to this research is by utilizing Gatterman's method first and then isolating the sulfinic acid by extraction with ether, extraction with sodium carbonate (10%) in order to obtain the sodium salt which is soluble in water, and then evaporating to dryness in order to obtain the dry sodium salt. This was necessary because it was found that the m-toluene sulfinic acid cannot be obtained in a pure state in the form of the free acid.

PROCEDURE

The following reactions were used to calculate the quantities of materials which were needed in the preparation of the m-toluene sulfinic acid.

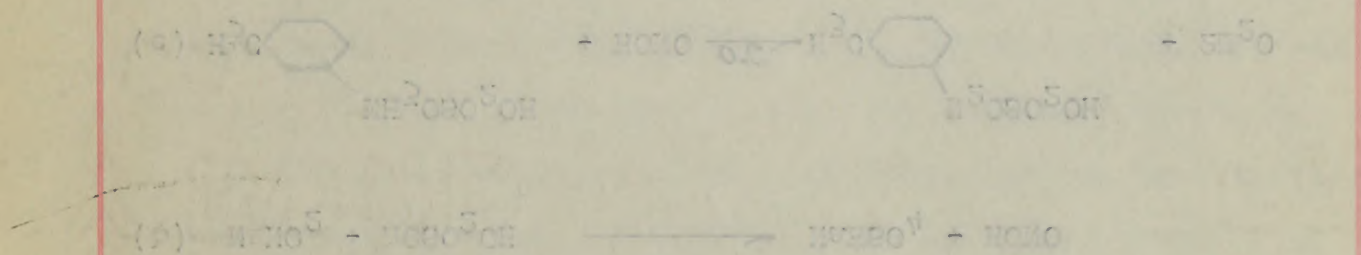






Ten grams of m-toluidine were dissolved in 40 grams of sulfuric acid and 250 grams of water in the reaction vessel. A large excess of acid and a dilute aqueous solution was used in the preparation of the m-toluene sulfinic acid. This was done also by Trȍger and Hille (1). The solution was cooled to 0°C by means of an ice and salt mixture and the m-toluidine was diazotized by adding slowly 7 grams of sodium nitrite dissolved in 40 grams of water. The mixture was continuously stirred by means of a mechanical stirrer during the diazotization. After three fourths of the nitrite solution had been added the reaction mixture was tested with starch potassium-iodide paper to test for complete diazotization. The remainder of the nitrite solution was added slowly until the reaction product gave a

(1) Trȍger, J., and Hille, W., J. Pr. Chem. 71, 201-35 (1905)



permanent blue color with the starch potassium iodide paper after standing for five to ten minutes.

The solution of the diazonium salt was then saturated with sulfur dioxide gas from the supply tank after all the connections on the apparatus had been sealed tightly so that no gas could escape. The temperature of the reaction product was still kept at 0°C and after it had become saturated with sulfur dioxide, 10 grams of copper powder were added slowly to the reaction mixture. According to Trüger and Hille (1) the sulfur dioxide treatment should not be prolonged and the copper powder should be added before the formation of a red precipitate in the reaction vessel. This precaution was followed in the above procedure.

The m-toluene sulfinic acid was isolated by two methods, i.e. in the form of its ferric salt according to Thomas's method outlined on page 20 of this thesis, and by extracting the mixture from the reaction vessel with ether and then converting the other soluble m-toluene sulfinic acid into the sodium salt of the acid by treatment with sodium hydroxide or sodium carbonate solution. The sodium carbonate treatment has this advantage that carbon dioxide is liberated during the reaction of the conversion of the sulfinic acid into the sodium salt and thus indicates the end of the reaction, when carbon dioxide is no longer liberated.

In the latter method the sodium salt which is more soluble in water than in an ether solution was drawn off from the ether

(1) Trüger, J., and Hille, W., J. Pr. Chem. 71, 201-35. (1905)

layer. The water solution was evaporated in order to obtain the sodium salt of the m-toluene sulfinic acid in the dry state. One sample of the sulfinic acid was kept in the ether solution to be used later in the oxidation of the sulfinic into the sulfonic acid.

layer. The water solution was evaporated in order to obtain
the sodium salt of the m-toluene sulfonic acid in the dry state.
One sample of the sulfonic acid was kept in the ether solution
to be used later in the oxidation of the sulfonic into the
sulfonic acid.

OBSERVATIONS

The following facts were noted concerning the nature of the reaction for the preparation of m-toluene sulfinic acid as described above:

(a) The m-toluidine first formed a white solid when it was added to the sulfuric acid and water solution, and then slowly dissolved forming a light amber colored solution.

(b) This clear amber colored solution changed to a deep brown colored solution on diazotization.

(c) On the addition of sulfur dioxide to the reaction mixture the color of the diazonium solution changed slowly to a red color. As the solution became saturated with sulfur dioxide it changed to a beautiful dark red wine color.

(d) On the addition of copper powder to the reaction mixture resulting from (c) the color again changed to a sort of brownish colored sludge, mixed with some sort of a white precipitate.

(e) The evolution of nitrogen was not observed due to the fact that sulfur dioxide gas was bubbled continuously through the reaction mixture.

(f) A green solution and a brown precipitate were the final products of the reaction.

(g) In isolating the m-toluene sulfinic acid both the clear solution and the copper sludge obtained in (f) were extracted with ordinary technical ether. The colorless ether layer changed to a light brown color, giving evidence that

OBSERVATIONS

The following facts were noted concerning the nature of the reaction for the preparation of m-toluene sulfinic acid as described above:

(a) The m-tolusulfone first formed a white solid when it was added to the sulfuric acid and water solution, and then slowly dissolved forming a light amber colored solution.

(b) This clear amber colored solution changed to a deep brown colored solution on diazotization.

(c) On the addition of sulfur dioxide to the reaction mixture the color of the diazonium solution changed slowly to a red color. As the solution became saturated with sulfur dioxide it changed to a beautiful dark red wine color.

(d) On the addition of copper powder to the reaction mixture resulting from (c) the color again changed to a port of brownish colored sludge, mixed with some sort of a white precipitate.

(e) The evolution of nitrogen was not observed due to the fact that sulfur dioxide gas was bubbled continuously through the reaction mixture.

(f) A green solution and a brown precipitate were the final products of the reaction.

(g) In isolating the m-toluene sulfinic acid both the clear solution and the copper sludge obtained in (f) were extracted with ordinary technical ether. The colorless ether layer changed to a light brown color, giving evidence that

something was dissolving in the ether.

(h) The ether solution on treatment with a 10% solution of sodium hydroxide gave the soluble sodium salt.of the m-toluene sulfinic acid. On neutralizing the sodium hydroxide extract with dilute HCl in the cold in order to precipitate the free sulfinic acid a yellowish precipitate formed which turned brown on drying. The nature of this precipitate was not determined at this point in the research due to the small quantity formed but there is the possibility that it is the disulfoxide of m-toluene. This falls in line with the observation of Tröger and Hille. In order to avoid this difficulty the sulfinic acid was isolated as its iron salt.

(i) The reaction mixture when treated as described under the preparation of ferric paratoluene sulfinic acid on page 20 of this thesis furnished an orange yellow precipitate which resembled the ferric paratoluene sulfonate in appearance.

(j) The ferric salt was treated with a slight excess of ammonium hydroxide which precipitated the iron as ferric hydroxide and left the sulfinic acid in solution. When the solution of the sulfinic acid was acidified with concentrated HCl in the cold no m-toluene sulfinic acid was precipitated. When this liquid was evaporated on a water bath a very small quantity of red oil was formed. This seemed to indicate that the m-toluene sulfinic acid was not a solid like the p-toluene sulfinic acid but an oil.

(k) Working on this assumption in the next run a small

portion of the reaction mixture was extracted with ether. The ether was distilled off and a red oil was left in the distilling flask. This further indicated that the m-toluene sulfinic acid is an oil instead of a solid. The remainder of the reaction mixture was treated according to Thomas's method and the ferric m-toluene sulfonate was obtained. This was converted into the m-toluene sulfinic acid as described under (j). The yield of oil obtained was again so small that it could not be worked with very efficiently. Therefore the ether extraction method was again tried.

(l) When the reaction product from the next run was extracted with ether, the color of the ether solution again became brown.

(m) The ether was distilled off a small portion of the ether extract and a red oil was obtained.

(n) Another portion was treated by a mixture of solid carbon dioxide and ether in order to try to freeze the m-toluene sulfinic acid out of the ether solution. The oil did not freeze out of the ether solution.

(o) It was also observed that the red oil on treatment with a 10% solution of sodium carbonate did not all react to form the sodium salt which again indicated that the oil was not all pure sulfinic acid. There is the possibility that this side product is disulfoxide of m-toluene which was previously encountered in (h).

(p) It was also determined that the red oil does not de-

portion of the reaction mixture was extracted with ether. The ether was distilled off and a red oil was left in the distilling flask. This further indicated that the m-toluene sulfinic acid is an oil instead of a solid. The remainder of the reaction mixture was treated according to Thomas's method and the ferric m-toluene sulfinate was obtained. This was converted into the m-toluene sulfinic acid as described under (j). The yield of oil obtained was again so small that it could not be worked with very efficiently. Therefore the ether extraction method was again tried.

(l) When the copper sludge and the clear solution from the next run were extracted with ether, the color of the ether solution again became brown.

(m) The ether was distilled off a small portion of the ether extract and a red oil was obtained.

(n) Another portion was treated by a mixture of solid carbon dioxide and ether in order to try to freeze the m-toluene sulfinic acid out of the ether solution. The oil did not freeze out of the ether solution.

(o) It was also observed that the red oil on treatment with a 10% solution of sodium carbonate did not all react to form the sodium salt which again indicated that the oil was not all pure sulfinic acid. There is the possibility that this side product is disulfoxide of m-toluene which was previously encountered in (h).

(p) It was also determined that the red oil does not de-

compose on standing in ether solution as long as the container is sealed tight.

compare on standing in other solution as long as the container is sealed tight.

DERIVATIVE OF M-TOLUENE SULFINIC ACID

In order to prove that the sodium salt of m-toluene sulfinic acid was obtained, the amide derivative of m-toluene sulfinic acid was prepared according to the method outlined by Mullikan (1). The m-toluene sulfonyl chloride was first prepared and was found to be a yellow oil.. The sulfonyl chloride was then converted into its corresponding amide which was found to melt between 106-107° C. The melting points given in the literature for this amide ranges from 106- to 108°C. In preparing this derivative the quantities used in Mullikan were doubled.

The procedure is as follows: "(a) Acid chlorides. Mix thoroughly by grinding about half a gram of the well-dried acid or one of its metallic salts, and about one and one half times the chemically equivalent quantitity of phosphorus pentachloride. Warm for some time at or below the temperature of boiling water, if this temperature is sufficient to cause reaction, until the reaction is completed. Wash the residue with small quantities of ice cold water to destroy the excess of reagent and remove the bi-product of the reaction, if it is sufficiently stable to permit such treatment." The product obtained from the above procedure was extracted with ordinary technical ether in order to extract the acid chloride of m-toluene sulfinic acid. The ether was distilled off to obtain the pure oil.

In order to convert it into the acid amide the following

(1) Mullikan, S.P., "Identification of Pure Organic Compounds," p. 14, Vol. IV. John Wiley and Sons, Inc. (1922)

procedure was used: "(b) Acid Amides. To prepare the acid amide boil the acid chloride obtained in paragraph (a) for a few minutes with twenty parts of concentrated aqueous ammonia. Evaporate to dryness on a water bath in a small glass capsule, and recrystallize the residue from boiling water or dilute alcohol, until it assumes a constant melting point."

OXIDATION OF ORGANIC COMPOUNDS

The following terms are used to describe the class of chemical reactions known as oxidation-reduction reactions. Oxidation (1) is the increase in positive valence of an element or a radical; and reduction is the decrease in positive valence of an element or radical. "Oxidation and reduction must evidently take place simultaneously, for in any reaction of this type the oxidising agent is always reduced, and the reducing agent is always oxidised." An oxidising agent is a substance capable of losing electrons and a reducing agent is a substance capable of gaining electrons. It is also known that oxidation and reduction reactions can be carried out in either a wet or dry way; i.e. either in the presence or absence of water (2).

According to Adkins and McElvain (3) the oxidation of an organic compound may involve; "(a) addition of oxygen or of a hydroxyl group to an unsaturated linkage; (b) the removal of hydrogen; (c) the replacement of hydrogen or another atom by oxygen or a hydroxyl group; (d) the breaking of a carbon to carbon linkage and the subsequent addition of oxygen or a hydroxyl group." The following factors are also listed by Adkins and McElvain and must be taken into account when selecting an oxidising agent for a given reaction. "(a) The oxidising agent must be strong enough to accomplish the desired results; (b) it

---

(1) Hamilton, L.F. and Simpson, S.G., "Calculations of Quantitative Chemical Analysis," p. 119, McGraw, Hill Book Co., Inc. (1927)

(2) Carven, R.M., "Foundations of Chemical Theory," p. 239-41, Blackie and Sons. (1921)

(3) Adkins, H. and McElvain, S.M., "Practice of Organic Chemistry," p. 189-97, McGraw, Hill Book Co., Inc. (1925)

must be of such a nature that the reaction may be stopped at the desired stage; (c) it should furnish a minimum of side reactions; (d) it should be possible to separate the products of the oxidation and reduction from the organic product formed; (e) the reagent should be inexpensive, easily handled, and require as little apparatus as possible." "The solubilizing or power effect of the medium should also be considered."

A list of oxidising agents which are used in organic oxidation is given by Adkins and McElvain. The equations of a few of the oxidation reactions are given as follows:

(a) concentrated nitric acid.

$$2\ HNO_3 \longrightarrow 2\ NO_2 + H_2O + O$$

(b) dilute nitric acid.

$$2\ HNO_3 \longrightarrow 2\ NO + H_2O + 3O$$

(c) potassium permanganate

(1) $KMnO_4 + HOH \rightarrow KOH + 2MnO_2 + 3\ O$ (basic medium)

(2) $KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + 3H_2O + 5\ O$ (acid medium)

(3) neutral medium like (1)

Potassium permanganate is especially used in the oxidation of side chains of carbon ring compounds which are fairly resistant to oxidation. If an excess of potassium permanganate is used in the oxidation process, it may be removed by adding a little alcohol and warming, or with oxalic acid in an acid solution.

(d) sodium dichromate.

$$Na_2Cr_2O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3\,O$$

(e) chromic anhydride.

$$2CrO_3 + 3\,H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3H_2O + 3\,O$$

Other oxidixing agents are:

(f) sodium iodide, sodium hypobromite, sodium hypochlorite and bleaching powder.

(g) barium peroxide, lead peroxide and manganese dioxide in the presence of an acid.

(h) hydrogen peroxide decomposes into one mole of water and one atom of oxygen.

(i) silver oxide and mercuric oxide.

(j) the following compounds are used in an acid medium: arsenic acid, ferric chloride, sulfuric acid, perchlorates, Caro's acid and sodium persulfate.

OXIDATION OF P-TOLUENE SULFINIC ACID TO THE SULFONIC ACID

The ultimate object of this research is to prepare m-toluene sulfonic acid by the oxidation of the corresponding sulfinic acid. First p-toluene sulfinic acid was oxidised to the sulfonic acid in order to determine a suitable oxidising agent for oxidising the sulfinic acid before attempting to oxidise m-toluene sulfinic acid. It was found that p-toluene sulfinic acid was readily oxidised to the corresponding sulfonic acid by dilute solution of potassium permanganate (.015 gm. /cc.). The free p-toluene sulfonic acid however was not obtained but the potassium salt was prepared. The acid was identified by preparing the toluidide derivative of p-toluene sulfonic acid. The toluidide derivative melted between 116-117°C. The melting point given in the literature ranges between 117-118°C. The free p-toluene sulfonic acid could not be isolated at this point in the research due to certain complications which are caused by the solubility of the sulfonic acid. The acid and salt (KCl) formed when trying to convert the potassium salt of the sulfonic acid into the free acid by treatment with dilute HCl were both soluble in most of the common solvents. However a suitable solvent has been found by the investigator to date and a method for isolating the free acid has also been suggested under the title of"possibilities for future research".

The oxidising agents which were used in this research in attempting to oxidise the p-toluene sulfinic acid to the sulfonic acid are listed and the results obtained are noted in

OXIDATION OF P-TOLUENE SULFINIC ACID TO THE SULFONIC ACID

The ultimate object of this research is to prepare m-toluene sulfonic acid by the oxidation of the corresponding sulfinic acid. First p-toluene sulfinic acid was oxidized to the sulfonic acid in order to determine a suitable oxidizing agent for oxidizing the sulfinic acid before attempting to oxidize m-toluene sulfinic acid. It was found that p-toluene sulfinic acid was readily oxidized to the corresponding sulfonic acid by dilute solution of potassium permanganate (.015 gm. \cc.). The free p-toluene sulfonic acid however was not obtained but the potassium salt was prepared. The acid was identified by preparing the toluidide derivative of p-toluene sulfonic acid. The toluidide derivative melted between 116-117°C. The melting point given in the literature ranges between 117-118°C. The free p-toluene sulfonic acid could not be isolated at this point in the research due to certain complications which are caused by the solubility of the sulfonic acid. The acid and salt (KOI) formed when trying to convert the potassium salt of the sulfonic acid into the free acid by treatment with dilute HOI were both soluble in most of the common solvents. However a suitable solvent has been found by the investigator to date and a method for isolating the free acid has also been suggested under the title of "possibilities for future research."

The oxidizing agents which were used in this research in attempting to oxidize the p-toluene sulfinic acid to the sulfonic acid are listed and the results obtained are noted in

the following discussion:

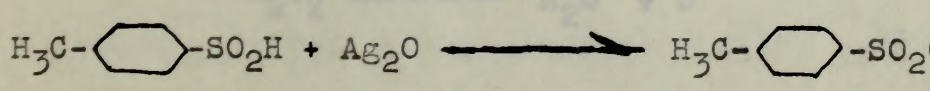
(a) Effect of air.— A small amount of p-toluene sulfinic acid was exposed to the atmosphere for several days in order to determine the effect of air. The p-toluene sulfinic acid was tested by Smiles' test (see page 35) before and after exposure. The p-toluene sulfinic acid gives a blue-purple color with Smiles' test. Any change in the sulfinic acid would cause a change in the intensity of this color. Thus the change could be easily noted by comparing with a standard made from the pure sulfinic acid. After exposure it was found that the color reaction was changed to a brownish color. This gave evidence that the sulfinic acids are partially oxidised by the air. However some of the sample retained the property of being insoluble in cold water, therefore it was concluded that the sulfinic acids are slowly oxidised by exposure to air.

(b) Oxidation with silver oxide.— Silver oxide was tried because it is easily reduced by many organic and inorganic compounds. The silver oxide was prepared from the reaction of silver nitrate and sodium hydroxide which is as follows:

$$2AgNO_3 + 2\ NaOH \longrightarrow 2\ AgOH + 2\ NaNO_3$$

$$2\ AgOH \longrightarrow Ag_2O + H_2O$$

The silver oxide obtained was washed with water until the washings gave no test for the silver ion on treatment with dilute HCl. The reaction for the preparation of the sulfonic acid by the use of silver oxide is theoretically as follows:



A 2 gram sample of p-toluene sulfinic acid was intimately mixed with 3.5 grams of moist silver oxide in the dark. This was allowed to stand in the dark for two hours with occassional stirring. The resulting mixture was then washed with water to dissolve any of the soluble silver p-toluene sulfonate which might have been formed. This water solution was then acidified with dilute HCl in order to precipitate the silver as silver chloride. The resulting silver chloride was filtered off and the filtrate was evaporated to dryness.

When the filtrate was evaporated to dryness a small amount of solid matter was obtained but it was slightly charred due to the presence of a little excess HCl which was used to precipitate the silver. This method was therefore discontinued until a suitable solvent could be found for the p-toluene sulfonic acid.

(c) Effect of oxygen gas.-- Tank oxygen was bubbled through a mixture of 1 gram of p-toluene sulfinic acid and water. There was no evidence that oxidation took place. It is possible that the p-toluene sulfinic acid can be oxidised in this way if a suitable catalyst is used and the reaction mixture stirred continuously.

(d) Oxidation with hydrogen peroxide.-- It is known that hydrogen peroxide is unstable and decomposes into oxygen and water according to the following reaction:

$$H_2O_2 \longrightarrow H_2O + O$$

It has been shown experimentally that the rate of decomposition of hydrogen peroxide is increased in the presence of sunlight or a suitable catalyst like metallic nickel or by the contact action of manganese dioxide or charcoal. A 3% solution of hydrogen peroxide was used as the oxidising agent.

A one gram sample of p-toluene sulfinic acid was mixed with an excess of hydrogen peroxide (30 cc.) and a small amount of nickel was used as a catalyst. The mixture was warmed and placed in the sunlight.

There was evidence of the evolution of gas and a small amount of the p-toluene sulfinic acid became soluble in the water solution which indicated that there was some oxidation. The greatest portion of the sulfinic acid remained insoluble. It is possible that the hydrogen peroxide used was too weak. Therefore the use of a 30% solution of hydrogen peroxide is suggested, by this investigator for later work. This method is worth developing because no side products would be formed during the process of oxidation and the pure p-toluene sulfonic acid could be obtained by merely evaporating the final solution and precipitating the acid.

(e) Oxidation with barium peroxide.— Barium peroxide decomposes in the presence of an acid to yield the barium salt of the acid and oxygen. In theory p-toluene sulfinic acid should be oxidised by barium peroxide according to the following equations:

1). 2 H_3C- -SO_2H + BaO_2 ⟶ $(H_3C$- -$SO_2)_2Ba$ + H_2O_2

2). $(H_3C\text{-}C_6H_4\text{-}SO_2)_2Ba + 2H_2O_2 \longrightarrow (H_3C\text{-}C_6H_4\text{-}SO_3)_2Ba + 2\,H_2O$

A little larger quantity of the p-toluene sulfinic acid was used in this procedure than in the oxidation with hydrogen peroxide.

A 2 gram sample of p-toluene sulfinic acid was mixed with 1.1 grams of barium peroxide in water. The reaction mixture was warmed on a hot water bath to speed up the reaction. After the reaction had ceased the mixture was allowed to stand for half an hour with occassional stirring. The reaction product was then filtered to remove any unreacted materials. The clear solution obtained was treated with dilute sulfuric acid in order to precipitate the barium as barium sulfate. The insoluble barium sulfate was filtered off and the clear filtrate was evaporated on a water bath.

On evaporation of this filtrate a residue was obtained which was slightly charred by the sulfuric acid in the solution. A few crystals however were obtained. They were in the form of monoclinic needles which closely resembled a crystal of pure p-toluene sulfonic acid.

This method was discontinued since a suitable solvent for the p-toluene sulfonic acid had not yet been found at this point in the research.

(f) Oxidation with potassium permanganate.— As previously stated potassium permanganate is often used to oxidise organic compounds. It was also illustrated by chemical equa-

2). $(H_3C-C_6H_4-SO_3)_2Ba + 2H_2O_2 \longrightarrow (H_3O-C_6H_4-SO_3)_2Ba +$

$2\ H_2O$

A little larger quantity of the p-toluene sulfinic acid was used in this procedure than in the oxidation with hydrogen peroxide.

A 2 gram sample of p-toluene sulfinic acid was mixed with 1.1 grams of barium peroxide in water. The reaction mixture was warmed on a hot water bath to speed up the reaction. After the reaction had ceased the mixture was allowed to stand for half an hour with occasional stirring. The reaction product was then filtered to remove any unreacted materials. The clear solution obtained was treated with dilute sulfuric acid in order to precipitate the barium as barium sulfate. The insoluble barium sulfate was filtered off and the clear filtrate was evaporated on a water bath.

On evaporation of this filtrate a residue was obtained which was slightly charred by the sulfuric acid in the solution. A few crystals however were obtained. They were in the form of monoclinic needles which closely resembled a crystal of pure p-toluene sulfonic acid.

This method was discontinued since a suitable solvent for the p-toluene sulfonic acid had not yet been found at this point in the research.

(2) Oxidation with potassium permanganate.-- As previously stated potassium permanganate is often used to oxidize organic compounds. It was also illustrated by chemical equa-

tions that three oxygens are furnished by potassium permanganate in a basic medium and 5 oxygen atoms in an acid medium. In the oxidation of p-toluene sulfinic acid in this research it was found that the reaction took place in an acid medium by testing the reaction mixture with litmus paper at different time intervals during the reaction. On the addition of potassium permanganate solution to the p-toluene sulfinic acid, the potassium was decolorized, which indicated that oxidation was taking place.

Instead of weighing out a calculated amount of potassium permanganate it was found that a dilute solution of the potassium permanganate could be added slowly to a sample of the sulfinic acid until the reaction was completed. This was indicated when a permanent purple color was imparted to the reaction mixture. This is in reality a titration method, and it could be used as a method for the estimation of the sulfinyl group ($-SO_2H$). An approximately 0.5 N solution of potassium permanganate was made up and used to oxidise the p-toluene sulfinic acid.

A 3 gram sample of p-toluene sulfinic acid was mixed with 10 cc. of water in a 250 cc. Erlenmeyer flask. The potassium permanganate solution was added slowly to the flask which was shaken after each addition. The permanganate solution was added to the reaction mixture until a faint purple color persisted. The color was removed by warming the reaction mixture with a few drops of alcohol. After the permanganate color was removed the reaction mixture was filtered and the filtrate

was evaporated to dryness. The dry residue obtained was assumed to be either the potassium or manganese salt of p-toluene sulfonic acid. In order to test for the manganese ion, a little of the dry salt was treated with a solution of sodium bismuthate in acetic acid. The purple color of the permanganate soluti n was not obtained, therefore it was concluded that the salt was the potassium salt of p-toluene sulfonic acid. There was no attempt made in this method to isolate the free sulfonic acid due to the difficulties encountered in the other procedures.

DERIVATIVE OF P-TOLUENE SULFONIC ACID

In order to prove that the salt of p-toluene sulfonic acid was prepared the toluidide derivative of p-toluene sulfonic acid was prepared. This derivative was found to melt between 116-117°C. The melting points given in the literature are 117-118°C. This derivative was prepared according to the method outlined by Kamm (1). It was found best to double the amounts of the reacting substances given by Kamm. It was also found that it was necessary to digest the mixture of the reacting substances for at least one hour and not 30 minutes as stated by Kamm. It was also necessary to add a few glass beads (cleaned with hot chromic acid) to the test tube in which the reaction was carried out in order to prevent bumping. The procedure given by Kamm is as follows: "Preparation of p-toluidides.-- In a dry test tube, mix 1 gm. of p-toluidine, 0.4 gm. of the powdered sodium salt, and 0.4 cc. of concentrated HCl. Boil the mixture very gently over a very small gas flame during 15 to 30 minutes. Cool, extract the reaction product with 5 cc. of boiling 95 per cent alcohol, pour into 50 cc. of hot water contained in a beaker, and boil down to a volume of about 10 cc. Filter the hot solution through a small filter paper in a heated funnel, crystallize the toluidide from the filtrate, dry and take its melting point. Sometimes recrystallization is necessary."

(1) Kamm, Ø., "Qualitative Organic Analysis," p. 177, John Wiley & Sons, Inc., (1932)

DERIVATIVE OF P-TOLUENE SULFONIC ACID

In order to prove that the salt of p-toluene sulfonic acid was prepared the toluamide derivative of p-toluene sulfonic acid was prepared. This derivative was found to melt between 116-117°C. The melting points given in the literature are 117-118°C. This derivative was prepared according to the method outlined by Kamm (1). It was found best to double the amounts of the reacting substances given by Kamm. It was also found that it was necessary to digest the mixtures of the reacting substances for at least one hour and not 30 minutes as stated by Kamm. It was also necessary to add a few glass beads (cleaned with hot chromic acid) to the test tube in which the reaction was carried out in order to prevent bumping. The procedure given by Kamm is as follows: "Preparation of p-toluamides.-- In a dry test tube, mix 1 gm. of p-toluidine, 0.4 gm. of the powdered sodium salt, and 0.4 cc. of concentrated HCl. Boil the mixture very gently over a very small gas flame during 15 to 30 minutes. Cool, extract the reaction product with 5 cc. of boiling 95 per cent alcohol, pour into 50 cc. of hot water contained in a beaker, and boil down to a volume of about 10 cc. Filter the hot solution through a small filter paper in a heated funnel, crystallize the toluamide from the filtrate, dry and take its melting point. Sometimes recrystallization is necessary."

(1) Kamm, O., "Qualitative Organic Analysis," p. 177, John Wiley & Sons, Inc., (1932)

OXIDATION OF M-TOLUENE SULFINIC ACID TO THE SULFONIC ACID

M-toluene sulfinic acid was oxidised in the same manner as the p-toluene sulfinic acid by barium peroxide and potassium permanganate as described on pages 52 and 53. In oxidising the m-toluene sulfinic acid by barium peroxide the same difficulty was encountered as in the oxidation of the p-toluene sulfinic acid, i.e. on attempting to isolate the free acid from the barium salt.

In oxidising the m-toluene sulfinic acid with a potassium permanganate solution, it was found that the permanganate solution was decolorized, which gave evidence that oxidation was taking place. The method of titrating the m-toluene sulfinic acid with potassium permanganate solution was found to be very convenient in this procedure,, because at this stage of the research there was no definite means for determining the amount of m-toluene sulfinic acid actually taken as a sample. It has been previously shown that the m-toluene sulfinic acid is a red oil. It was also stated that this red oil was not all m-toluene sulfinic acid. This was confirmed during the process of oxidising the m-toluene sulfinic acid with potassium permanganate, since a yellowish brown resinous by-product was produced during the oxidation. The exact nature of this compound was not determined at this stage of the research. The salt of the m-toluene sulfonic acid was also obtained by this method.

OXIDATION OF M-TOLUENE SULFINIC ACID TO THE SULFONIC ACID

M-toluene sulfinic acid was oxidized in the same manner as the p-toluene sulfinic acid by barium peroxide and potassium permanganate as described on pages 52 and 53. In oxidizing the m-toluene sulfinic acid by barium peroxide the same difficulty was encountered as in the oxidation of the p-toluene sulfinic acid, i.e. on attempting to isolate the free acid from the barium salt.

In oxidizing the m-toluene sulfinic acid with a potassium permanganate solution, it was found that the permanganate solution was decolorized, which gave evidence that oxidation was taking place. The method of titrating the m-toluene sulfinic acid with potassium permanganate solution was found to be very convenient in this procedure, because at this stage of the research there was no definite means for determining the amount of m-toluene sulfinic acid actually taken as a sample. It has been previously shown that the m-toluene sulfinic acid is a red oil. It was also stated that this red oil was not all m-toluene sulfinic acid. This was confirmed during the process of oxidizing the m-toluene sulfinic acid with potassium permanganate, since a yellowish brown resinous by-product was produced during the oxidation. The exact nature of this compound was not determined at this stage of the research. The salt of the m-toluene sulfonic acid was also obtained by this method.

DERIVATIVE OF M-TOLUENE SULFONIC ACID

In order to prove that m-toluene sulfinic acid had been oxidised to the sulfonic acid, the salt of the m-toluene sulfonic acid was converted into the sulfonyl chloride and then into the amide. The amide was prepared according to the directions given on pages 44-45 of this thesis. This amide derivative of the m-toluene sulfonic acid melted between 105-107 C. The melting points of this compound given in the literature range from 106-108 C.

DERIVATIVE OF M-TOLUENE SULFONIC ACID

In order to prove that m-toluene sulfinic acid had been oxidized to the sulfonic acid, the salt of the m-toluene sulfonic acid was converted into the sulfonyl chloride and then into the amide. The amide was prepared according to the directions given on pages 44-45 of this thesis. This amide derivative of the m-toluene sulfonic acid melted between 105-107 C. The melting points of this compound given in the literature range from 106-108 C.

SOLUBILITY TABLE OF P-TOLUENE SULFONIC ACID

Solvent	Hot	Cold
N-butyl ether	soluble	insoluble
water	soluble	soluble
benzene	slightly soluble	insoluble
acetone	very soluble	soluble
ligroin	v. slightly sol.	v. slightly sol.
carbon tetrachloride	" " "	" " "
chloroform	" " "	" " "
carbon disulfide	" " "	" " "
technical ether	very soluble	soluble

This table shows that N-butyl ether will serve as a suitable solvent for p-toluene sulfonic acid.

POSSIBILITIES FOR FUTURE RESEARCH

The following possibilities for future research are listed in order to help lay the foundation for further work in the preparation of the isomeric toluene sulfonic acids.

(a) The following theory for the formation of the sulfinic acids is postulated by this investigator: that in the preparation of sulfinic acids sulfurous acid acts as a strong reducing agent and removes oxygen from the diazonium salt and is itself oxidised to sulfuric acid. Therefore it is proposed that the oxidation-reduction potentials of the sulfurous acid and diazonium salt be determined in order to prove whether the above postulate is correct or not.

(b) In the preparation of m-toluene sulfinic acid it was found that a side product was formed which dissolved in ether together with the m-toluene sulfinic acid in the isolation of this acid by ether extraction. Some of this material has been retained by this investigator after extracting the m-toluene sulfinic acid as its sodium salt from the ether solution. It has been suggested that this substance is the disulfoxide of m-toluene. This offers the problem of obtaining this substance in a pure enough state so that it may be analyzed and identified.

(c) It is suggested that m-toluene sulfinic acid be prepared by the methods outlined on pages 19 through 23 of this thesis.

(d) It is suggested that the free p-toluene sulfonic acid

and m-toluene sulfonic acid be isolated by the following procedure. The salt of the sulfonic acid obtained from either the barium peroxide or potassium permanganate treatment should be neutralized with dilute HCl and thus obtain the free sulfonic acid and salt of the mineral acid in a water solution. The water solution should next be evaporated to dryness. The residue should then be extracted with hot N-butyl ether. The free sulfonic acid could then be obtained by distilling off the solvent.

SUMMARY AND CONCLUSIONS

The following facts are noted in this research:

(1) A resume of the literature is given in which the properties of the isomeric sulfonic acids are given and the methods for their preparation. Methods for the preparation of the sulfinic acids are also given.

(2) P-toluene sulfinic acid was prepared in this research by a combination of Gatterman's method for the preparation of sulfinic acids and Thomas's method for the isolation of sulfinic acids.

(3) The potassium salt of p-toluene sulfonic acid was prepared by the oxidation of p-toluene sulfinic acid with a dilute solution of potassium permanganate. This was identified as the toluidide of p-toluene sulfonic acid.

(4) M-toluene sulfinic acid was prepared and isolated as its sodium salt. This was identified as the amide of m-toluene sulfinic acid.

(5) M-toluene sulfonic acid was prepared as its potassium salt.

(6) Possibilities for future research work are given in this thesis.

(7) Therefore this thesis proves that m-toluene sulfonic acid can be prepared from m-toluidine.

SUMMARY AND CONCLUSIONS

The following facts are noted in this research:

(1) A resume of the literature is given in which the properties of the isomeric sulfonic acids are given and the methods for their preparation. Methods for the preparation of the sulfinic acids are also given.

(2) P-toluene sulfinic acid was prepared in this research by a combination of Gattermann's method for the preparation of sulfinic acids and Thomas's method for the isolation of sulfinic acids.

(3) The potassium salt of p-toluene sulfonic acid was prepared by the oxidation of p-toluene sulfinic acid with a dilute solution of potassium permanganate. This was identified as the tolutide of p-toluene sulfonic acid.

(4) M-toluene sulfinic acid was prepared and isolated as its sodium salt. This was identified as the amide of m-toluene sulfinic acid.

(5) M-toluene sulfonic acid was prepared as its potassium salt.

(6) Possibilities for future research work are given in this thesis.

(7) Therefore this thesis proves that m-toluene sulfonic acid can be prepared from m-tolutidine.

BIBLIOGRAPHY

Abbreviations

1. Ann.....Annalen der Chemie und Pharmacie.
2. Ber.....Berichte der Deutschen Chemisches Gesellschaft.
3. Chem. Zentr.....Chemisches Zentrablatt.
4. E.P.....English Patent.
5. J. Chem. Soc.....Journal of the Chemical Society. (London)
6. J. Pr. Chem.....Journal für Praktisch Chemie.

References

1. Adkins, H. and McElvain, S.M., "Practice of Organic Chemistry," p. 189-197, McGraw, Hill Book Co., Inc. (1925)
2. Bloomstrand, C.W., Ber. 9, 1584-7 (1876)
3. Brockman, C.J., "Electro-Organic Chemistry," p. 234-5, John Wiley & Sons, Inc. (1926)
4. Cain, J.C., "The Chemistry and Technology of the Diazo Compounds," p. 65, Edward Arnold & Co. (1920)
5. Carven, R.M., "Foundations of Chemical Theory," p. 239-41, Blackie and Sons. (1921)
6. Claissen, P. and Wallen, P., Ber. 12, 1848 (1879)
7. Clarke, H.T., "A Handbook of Organic Analysis," p. 57, Edward Arnold & Co. (1931)
8. Cohen, J.B., "Theoretical Organic Chemistry," p. 528, Macmillan and Co. (1928)
9. English Patent 26139 of 1896.
10. English Patent 12871 of 1900.
11. English Patent 7288 of 1906.
12. Fromm, E. and Erfurt, R., Ber. 42, 3821 (1909)

BIBLIOGRAPHY

Abbreviations

1. Ann.....Annalen der Chemie und Pharmacie.

2. Ber.....Berichte der Deutschen Chemischen Gesell-
schaft.

3. Chem. Zentr.....Chemischen Zentrablatt.

4. E.P.....English Patent.

5. J. Chem. Soc.....Journal of the Chemical Society. (London)

6. J. pr. Chem.....Journal für Praktisch Chemie.

References

1. Adkins, H. and McElvain, S.M., "Practice of Organic Chemistry," p. 189-197, McGraw, Hill Book Co., Inc. (1925)

2. Bloomstrand, C.W., Ber. 9, 1584-7 (1876)

3. Brockman, C.J., "Electro-Organic Chemistry," p. 234-5, John Wiley & Sons, Inc. (1926)

4. Cain, J.C., "The Chemistry and Technology of the Diazo Compounds," p. 65, Edward Arnold & Co. (1920)

5. Carven, R.M., "Foundations of Chemical Theory," p. 239-41, Blackie and Sons. (1921)

6. Claisen, P. and Wallen, P., Ber. 12, 1846 (1879)

7. Clarke, H.T., "A Handbook of Organic Analysis," p. 57, Edward Arnold & Co. (1921)

8. Cohen, J.B., "Theoretical Organic Chemistry," p. 528, Macmillan and Co. (1928)

9. English Patent 26139 of 1896.

10. English Patent 12871 of 1900.

11. English Patent 7288 of 1906.

12. Fromm, E. and Brunt, R., Ber. 42, 3821 (1909)

13. Gatterman, L., Ber. 24, 2011-21 (1891)

14. Gatterman, L., Ber. 32, 1136 (1899)

15. Gatterman, L., "Practical Methods of Organic Chemistry," p. 240-1, Macmillan Co. (1914)

16. Gatterman, L., and Wieland, H., "Laboratory Methods of Organic Chemistry," p. 183-4, Macmillan Co.. (1932)

17. Gewer, F., J.Chem. Soc., 27, p. 168 (1874)

18. Gutman, A., Ber. 41, 3351 (1908)

19. Gutman, A., Ber. 42, 480 (1909)

20. Holleman, H.F., "A Text Book of Organic Chemistry," p. 467, John Wiley & Sons, Inc. (1930)

21. Hübner, H. and Post, J., J. Chem. Soc. p. 56-60 (1874)

22. Hamilton, F.L. and Simpson, G.S., "Calculations of Quantitative Chemical Analysis," McGraw, Hill Book Co., Inc. (1927)

23. Kamm, O., "Qualitative Organic Analysis," p. 177, John Wiley & Sons, Inc. (1932)

24. Kingzett, C.T., "Chemical Encyclopedia," p. 924, P. Balliere, Tindall and Cox. (1932)

25. Knoevenagel, E. and Kenner, J., Ber. 41, 3315-22 (1908)

26. Knoevenagel, E. and Kenner, J., J. Chem. Soc. 83, 7541 (1908)

27. Lowy, A. and Harrow, B., "An Introduction to Organic Chemistry," p. 239, John Wiley & Sons, Inc. (1932)

28. Meister, Lucius, Brüning, Chem. Zntr. II, 513 (1910)

29. Müller, F.H. and Wiesinger, F., Ber. 12, 1348-9 (1879)

30. Mullikan, S.P., "Identification of Pure Organic Compounds," p. 14, Vol. IV. John Wiley & Sons, Inc. (1922)

31. Noyes, A.A., "Qualtiative Chemical Analysis," p. 60, Macmillan Co. (1920)

32. Otto, R., Ann. 142, 93 (1867)

33. Otto, R., Ber. 13, 1272 (1880)

34. Otto, R., J. Chem. Soc. 38, 810 (1880)

35. Otto, R. and Rossing, R., Ber. 19, 1224-7 (1899)

36. Peckman, H. Von., J. Chem. Soc. 28, p. 78 (1875)

37. Rosamund, K.W., Ber. 54, 438-40 (1921)

38. Richter, V. Von., "Organic Chemistry or Chemistry of the Carbon Compounds," Vol. II, p. 179-80, P. Blakiston's Son & Co., (1922)

39. Schiller, R. and Otto, R., Ber. 9, 1584-71 (1876)

40. Thomas, J., J. Chem. Soc. 95, 344 (1909)

41. Tröger, J. and Hille, W., J. Pr. Chem. 71, 201-35 (1905)

42. Watts, "Dictionary of Chemistry," p. 755-6, Longmans, Green & Co. (1894)

BOSTON UNIVERSITY
1 1719 02552 7583